

**Geological Evolution and Analysis of  
Confirmed or Suspected Gas Hydrate Localities**

**Volume 5. Gas Hydrates in the Russian Literature**

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## PREFACE

This document is Volume V of a series of reports entitled "Geological Evolution and Analysis of Confirmed or Suspected Gas Hydrate Localities." Volume V is an analysis of "Gas Hydrates in the Russian Literature." This report presents an assessment of gas hydrate research as documented in Russian literature. It presents material that includes regional and local settings, geological history, stratigraphy, and physical properties. It provides some necessary regional and geological background of major hydrate occurrences in Russia. This report provides a better understanding of the gas hydrate phenomena in Russia and gives a detailed accounting of gas production history from a gas hydrate field in Siberia. It provides an important assessment of the understanding of gas hydrate deposition and production.

Project Manager  
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## EXECUTIVE SUMMARY

Gas hydrates are ice-like substances which are formed by the physical entrapment of light hydrocarbon gas in water molecules under conditions of low temperature and high pressure. In nature such processes and conditions are known to occur under ice sheets, in porous rocks underlying permafrost, and at or below the sea floor. The high pressure and low temperature conditions can also be man-made. In some cases, such conditions occur where and when they are not desired, especially in gas pipelines and technical or technological facilities. In pipelines and related facilities gas hydrates clog the lines and cause severe technical problems.

Initially, the technical problems and later consideration of gas hydrates as an energy resource involved a great number of Russian engineers and scientists in serious theoretical investigations, laboratory and field tests, and exploration for the in situ gas hydrate deposits. These investigations have been continued and so far have resulted in the discovery of two major gas hydrate deposits. The Messoiakh gas hydrate field was discovered in 1967 in the northeastern part of western Siberia. Subsequently, the Vilyui gas hydrate field in the north-central part of Siberia was discovered. Thus, both deposits are located within the permafrost climatic zone and are directly related to underlying conventional type gas and oil fields.

The Messoiakh gas hydrate deposit was brought into production in 1969. Subsequently it encountered technological problems and in 1978 production was ceased; it was resumed again in 1981 (Makogon, 1984; Trofimuk et al., 1984).

Both gas hydrate deposits (i.e. Messoiakh and Vilyui) have been thoroughly studied and many scientists have used them as testing grounds. In conjunction with these and other research programs Russian scientists have published a great number of articles, papers and books, which mostly concern the technical and technological problems related to and/or caused by gas hydrates. However, because of the considerable difficulties in access to many publications (originally restricted circulation or unavailable in the U.S.) this report is based on the information and data included in the references cited. Although even this appears to be a great number, much of the material was summarized in the outstanding book by Makogon entitled

**Hydrates of Natural Gas** (originally published in 1974, then reprinted in English in 1978 and 1981).

Specifically, the thermodynamics and kinetics of hydrate formation, determination of thermal and pressure environments that are considered favorable for gas hydrate formation, stability and dissociation, assessment of potential reserves of natural gas occurring as hydrates, exploration and production methods, are the subjects discussed in numerous Russian publications, and all are topics discussed in this report.

Review of relevant Russian literature confirmed that strong efforts have been made since the early 1960s, particularly in the theoretical and experimental field of gas hydrates. These efforts were oriented toward the assessment of various factors critical in gas hydrate formation, stabilization, and conditions for dissociation. The experiments performed in the Gubkin Petrochemical and Gas Industry Institute in Moscow considerably improved the understanding of the mechanism steering the gas hydrate crystallization processes. Besides various thermodynamic conditions under which gas hydrates form, Russian scientists have also considered in their studies the role of a porous environment versus water-gas interface, the availability of gas in the gas hydrate formation zone, gas composition, relative gravity of gas, geometry of porous space, gas diffusion processes, rate of cooling, etc. Each of these factors alters the pressure-temperature equilibrium conditions of gas hydrates. The experimental results of the relationships between various factors and gas hydrate formation are demonstrated in this report in numerous diagrams. The data shown in the diagrams have a qualitative meaning and application. They provide an explanation for the various phases of gas hydrate formation under diverse conditions. For some practical purposes (e.g. calculation of gas reserves in hydrate deposits) kinetic processes of the hydrate formation are still inadequately known. According to Russian authors (Barkan and Voronov, 1982) a high discovery potential and development of the economically viable gas reserves strongly encourages further investigations in the area of gas hydrates.

At the present time, field data on gas hydrate deposits constitutes invaluable information which enables the verification of accumulated theoretical and experimental results. Thus, the importance of published data from the two known major continental gas hydrate deposits, the Messoikh and Vilyui fields, is apparent.

It appears that the discovery of the Messoikh gas hydrate deposit was quite accidental. The production tests of the prolific oil and gas Dolgan Sandstones of the Albian-Cenomanian in the Messoikh field showed unusually low gas yields from the top intervals of an otherwise excellent reservoir (average porosity 25%, permeability 125 md; Sheshukov et al., 1972). The gas hydrate presence in this field provided a satisfactory explanation for the anomalous gas yields. Indeed, further tests proved that the upper part of the Messoikh oil and gas field lies within the stability zone of gas hydrates. It has been proven that the lower boundary of the hydrate zone coincides with the 10°C (50°F) geoisotherm while the formation pressure is close to the hydrostatic

(approximately 7.8 MPa). In the thermal profile of the Messoiakh field the bottom of the permafrost is easily recognizable at a depth of approximately 400 m.

After the gas hydrates had been taken into account the total gas reserves of the Messoiakh increased from  $18 \times 10^9 \text{ m}^3$  (0.63 TCF) to  $80 \times 10^9 \text{ m}^3$  (2.8 TCF).

Unprecedented gas production from the Messoiakh hydrate deposit was carried out since 1969 with technically necessary interruptions. The applied techniques of releasing gas from the hydrates consisted of depressurization and inhibition (mainly with methanol) of the gas hydrates at the base of the hydrate zone. During 1969 - 1983 gas production activities, more than  $5 \times 10^9 \text{ m}^3$  ( $1.8 \times 10^{11}$  CF) of gas had been released from the hydrate phase (Makogon, 1984). The maximum annual gas production in the Messoiakh field of  $2.1 \times 10^9 \text{ m}^3$  ( $7.4 \times 10^{10}$  CF, 200 MMCFD) was attained in 1972.

The Vilyui gas hydrate field is also closely related to a conventional type of gas deposit.

Russian authors (Makogon, 1973; Trofimuk et al., 1979) suggest the possibility of conventional hydrocarbon occurrences in trapping systems formed by upward shifted hydrate zones in the transitional zones between the continental and marine environments in the polar regions.

Marine gas hydrates have limited documentation in Russian literature. There are only scientific notes about the recovery of gas hydrates in cores from the bottom sediments of the Black Sea (Yefremova and Zhizhchenko, 1972; station 116) and from an unspecified location in the Pacific Ocean (Makogon, 1974). Russian forecasts on marine gas hydrate reserves are based mainly on methane content in the sea bottom sediments and oceanographic data.

Estimates of gas reserves have been made by Trofimuk et al. (1981) and Cherskii and Tsarev (1977). Trofimuk and his co-workers estimate amounts  $57 \times 10^{12} \text{ m}^3$  (2,000 TCF) of total gas in the continental regions and  $5$  to  $25 \times 10^{15} \text{ m}^3$  (1,800 - 8,800 TCF) of gas in the marine type of gas hydrate deposits of the continental shelf and slope.

Exploration methods for deposits of gas hydrates are presented by Russian authors in general terms. It seems that the exploration techniques are still at initial stages. Most frequently recommended are seismic surveys, geochemical methods, and well logging.

The methodology of calculation of gas hydrate reserves in gas hydrate deposits is another frequently discussed subject. Because kinetic processes of gas hydrate deposit formation and further evolution are not entirely known, gas reserves can only be assessed at an estimated level. The proposed methods for assessment of continental gas hydrate deposits are based on calculations of the initial gas content in water, before gas hydrates are formed, and the amount of gas which enters the hydrate zone in process of its evolution. The example of such an estimate was presented by Cherskii et al. (1976) for the Vilyui Syncline.

The calculation of gas reserves in marine gas hydrate deposits is more complex. Cherskii and Tsarev (1977) calculated net biogenic methane in the marine sediments for various geomorphologic zones.

Subsequently, these authors assumed that only 1% of biogenic methane enters the hydrate zone. Thus, only this latter amount of biogenic gas was considered for calculation of gas reserves in marine hydrates.

Besides the above mentioned areas of expertise and achievements, Russians already have considerable experience in the development and production of gas from hydrate deposits. Because gas hydrates are considered as an alternative energy resource, the development and production methods are of particular importance.

In the Messoiakh field, depressurization and gas hydrate inhibition techniques have been applied. Strong scientific efforts are being made toward developing less expensive inhibitors than the currently used methanol. Use of hot brines from the adjacent strata appears to be at a research stage.

Gas production from marine hydrates requires the development of new methods. Russian authors suggest rubbing of the hydrate-bearing sediment and suction of the slurry containing sediment and partially dissociated hydrates to the surface where the gas would be separated.

Besides the production experience, two Russian authors (Barkan and Voronov, 1982) recently expressed the opinion that a significant technological breakthrough must be made before gas production could be carried out on a larger industrial scale. Nonetheless, most of the Russian engineers and scientists are optimistic about the future of gas hydrates as an energy resource and strongly recommend the confirmation of further aggressive research in this field.

This report is a part of a much larger study of the geological environments and occurrences of gas hydrates, currently underway by Geoexplorers International, Inc. for the U.S. Department of Energy - Morgantown Energy Technology Center.

## INTRODUCTION

Russian scientists have contributed a great wealth of direct observation, analytical data, and concepts pertaining to the formation and stability of gas hydrates, viewing them as "huge energy resources." All this information has come from extensive and diverse studies involving various research institutions and a great number of scientific and professional workers. Originally, the results of their studies were mostly oriented toward preventing the technical problems that had been encountered during pipeline gas transportation, especially through the arctic regions of Siberia.

In the 1960s strong encouragement for the study of hydrates came with the discovery of gas hydrate deposits in the Messoikh and Vilyui fields. These were accompanied by an increased number of publications, concerning mainly laboratory research, tests, and field observations performed in both locations with the gas hydrate deposits (Messoikh and Vilyui).

The economic importance of the hydrate deposits as a potential resource of energy encouraged the Russian scientists to make continuous efforts toward better understanding of the hydrate phenomenon and developing techniques of exploration and production. However, most of the Russian publications on gas hydrates are related to prevention of their occurrence in pipeline facilities and gas wells. Much of the research results could be applied to more precise determination of gas hydrate formation and stability in natural environments.

Gas hydrate formation and stability in natural environments are the main objectives of this and a much larger study mandated to Geoexplorers International, Inc. by the U.S. Department of Energy, Morgantown Energy Technology Center (DOE-METC). This report is organized into the topics which are most often addressed in the Russian literature; and, therefore, it includes discussion on the basic knowledge of gas hydrates as well as on its practical applications, namely:

- Structural features of gas hydrates,
- Hydrocarbon generation and gas solubility in water,
- Natural gas hydrate formation,
- Exploration methods for natural gas hydrate deposits,
- Occurrence of natural gas hydrates,
- Natural gas hydrate reserves, and
- Development of natural gas hydrate deposits.

Each of these topics reflects on the priorities, methodology and the results obtained by Russian scientists. Cited references reveal the institutions and degree of involvement of particular authors in the subject investigated.

In some sections of this report, the literature references show the names of non-Soviet scientists who contributed and still have leading recognition in certain areas of gas hydrates. In these cases, the investigations were initiated and are more advanced outside of the Soviet Union (USSR). Especially, the non-Soviet authors are referenced when the results of their investigations are extensively used by Soviet authors.

It appears that Russian priorities in the subject of natural gas hydrates have been focused on research into gas hydrate kinetics and thermodynamics. The publications pertaining to continental (onshore) hydrates greatly outnumber those on hydrates generated in the marine environments, which clearly indicates the direction of Soviet interests in the field.

Although this study is based on readily available Russian literature, many references cited in Russian publications are available for internal use only; the authors of this report are confident that it adequately represents the up-to-date knowledge and major directions of Russian research and developments in the domain of gas hydrate deposits.

### Units and Terminology

In most of the studied literature, Russian authors use  $\text{kgf/cm}^2$  as a pressure unit from c.g.s. (centimeter, gram, second) and m.k.s. (meter, kilogram, second) sysem which may cause some discomfort to the readers accustomed to English unit systems. Conversion of the traditional pressure units used by the Russian authors to the S.I. (System International) could result in diminished precision of various data (i.e. double rounding, changing of grid, etc.). Therefore, the authors of this report choose to retain the units as they were originally presented in Russian publications. Readers who wish to convert the pressure values expressed in  $\text{kgf/cm}^2$  into Pa (Pascal; S.I.) may do so using the formula:

$$P(\text{Pa}) = P(\text{kgf/cm}^2) \times 98060$$

Otherwise, we have made special efforts and wherever it was possible the Russian geological terms are substituted with adequate terms used in English language professional literature (with the exception of "synclise" which is used in both languages, but Russians use it more frequently).

Unfortunately, the Russian authors report neither the scales nor coordinates of the maps. Rarely, maps or other graphical illustrations contain adequate reference points (i.e. cities, towns, names of the rivers, mountains or other location markers). Obviously, any map and/or geologic (or special) cross section without scale and coordinates cannot be considered as properly prepared. Therefore, wherever it was possible we have determined the scale and/or location (e.g. Messaiakh gas hydrate field).

## HISTORICAL REVIEW

An historical review of gas hydrate studies by Russian authors is already available in English (Y. F. Makogon, 1978 and 1981 - i.e. the same book had been published by Geoexplorers Assoc., Inc. and Pennwell Publishing Co., respectively). There are also other publications in English, which include references pertaining to the history of the development of knowledge in gas hydrates contributed by Russian authors (e.g., Berecz and Balla-Achs, 1983; Kuuskraa et al., 1983, U.S. Department of Energy, Morgantown Energy Technology Center, 1985).

Russians entered the gas hydrate field about 130 years after the first discovery by British chemist Davy (1811). In the meantime numerous scientists from western countries considerably advanced the initial understanding of gas hydrate formation and their nature. These studies were mostly theoretical (Faraday, 1823; Lowig, 1828; Schoenfeld, 1855; Roozenboom, 1884; de la Rive, 1829; Ditte, 1882; Duclaux, 1867; Tenrete, 1878). Hammerschmidt (1934) discovered that gas hydrates plug pipelines.

Also prior to Russian involvement in gas hydrate investigation, Deaton and Frost, working for the U.S. Bureau of Mines, published a series of articles pertaining to gas hydrate formation and properties (Deaton and Frost, 1937; 1938; 1940; 1946). Katz, another American scientist, was also involved in the broad range of the gas hydrate research and its practical applications (Katz, 1942, 1944).

In the Soviet Union in the late 1940s and 1950s, the rapidly developing gas pipeline transportation industry faced tremendous problems due to hydrate formation in the facilities located in severely cold climatic conditions, particularly in Siberia. Gas hydrates caused extensive damage to the pipelines. Thus, the technical problems were direct reasons and urgent needs for research on gas hydrates. The first information on gas hydrate research in published Russian literature was reported by Strizhev (1946; after Makogon, 1974), Mokhnatkin (1947; after Makogon, 1974) and Palvelev (1949; after Makogon, 1974). Strizhev predicted the presence of the hydrates in gas-bearing sedimentary rocks in northern regions of the Soviet Union. Mokhnatkin analyzed gas formation processes in the Earth's crust, and Palvelev suggested that hydrates should be present in coal deposits, where the temperature is below 25°C and pressure range from 700 to 900 kgf/cm<sup>2</sup>.

Also in the 1950s, in Germany, the United States and France, von Stackelberg, Muller, Claussen, Pauling and Marsh published numerous papers explaining the gas hydrate crystallographic structures. Van der Waals and Plateeuw had developed a model of the statistical mechanics of gas hydrates and published their results in 1959. The results of these investigations are extremely critical in understanding gas hydrate formation in natural and man-made environments. The gas hydrate structural features and the van der

Waals model have been extensively used by Russian researchers in their theoretical and practical investigations.

Strong efforts were also made in the 1950s in the Soviet Union toward more precise determination of the nature of gas hydrates through the use of contemporary analytical instrumentation. The leading scientific institution in the field was and still is the Gubkin Petrochemical and Gas Industry Institute (GPGII) in Moscow. The main objective of the research was to establish the relationships among the major factors critical in gas hydrate formation, specifically under conditions of free gas-water interface (i.e. in pipeline and related facilities).

In the 1960s research on gas hydrates, particularly in the areas of kinetics and thermodynamics, was expanded. Makogon (1974) reported that the thermodynamic studies conducted by Cherskii (1961) in Yakutia projected the presence of gas hydrates within the permafrost zone. Cherskii's theoretical studies were followed in 1963 with the drilling of a special exploratory well to the depth of 1,850 m. The presence of the permafrost zone has been confirmed as deep as 1,400 m below the ground surface.

In 1964 a team of scientists, including Vasilev, Makogon, Trebin, Trofimuk, and Cherskii discovered the Messoiakh gas hydrate deposit. It is noteworthy that this deposit in the north-eastern part of Western Siberia is directly related to and is located above a conventional natural gas field.

Discovery of the Messoiakh gas hydrate deposit further accelerated the ongoing research and exploration program. More scientists from scientific and industrial research institutions were involved in the expanded program. Besides Gubkin Petrochemical and Gas Industry Institute, various research programs on gas hydrates were carried out by the Geology Branch of the Soviet Union Academy of Sciences, the Thermal Physics Institute of the Siberian Branch of the Academy of Sciences, All-Soviet Union Scientific Research, the Petroleum Institute, and others. Still, most of the investigations were in the theoretical field of gas hydrate thermodynamics. Experimental laboratory and field tests were also performed. Experiments on gas hydrate formation in free gas-water interface and in porous environments were carried out in Gubkin Petrochemical and Gas Industry Institute. Basic relationships of the gas hydrate formation process, consistent with previous theoretical and experimental findings, were established. The results of these studies were published mainly by Makogon in 1965 and 1966. The newly discovered Messoiakh gas hydrate deposit played an important role in the rapidly growing knowledge of gas hydrates as a testing ground. Thermodynamic parameters determined in the Messoiakh deposit confirmed the results of previous theoretical scientific efforts (Makogon, 1978). Subsequently, the Vilyui gas hydrate deposit, also in Siberia, was discovered (Cherskii et al., 1976). The Messoiakh deposit was brought into production in 1969 and its peak was reached in 1972 (Makogon, 1984).

According to Makogon (1974) and the most recent publications, particularly by Barkan and Voronov (1983), there are numerous prospective regions with highly favorable potential for large reserves of gas hydrates in Siberia and within the continental margins, besides Messoiakh and Vilyui. An optimistic view of gas hydrates as an "enormous potential energy resource" was also officially confirmed by E. A. Kozlovsky, Minister, the USSR Ministry of Geology, during the opening ceremony of the 27th International Geological Congress, held in Moscow (4 - 14 August, 1984).



Very extensive theoretical studies, laboratory experiments and direct observations in the field, carried out by many Russian scientists and professionals of various disciplines, resulted in numerous publications, including a great variety of scientific articles, papers and books. Although a large number of publications and authors involved do not necessarily represent advancement of knowledge of the subject field, it reflects on the interest and activity in research and exploration, and certainly practical needs of their results. An approximate number of publications (disregarding their length and the subject fields concerned) published in various years are shown in Figure 1. Generally, it appears that most of the published data and the analytical discussions pertain to the kinetics and thermodynamics of gas hydrates. There are also numerous publications pertaining directly to the above mentioned gas hydrate deposits, but their evaluation and detailed geological description will be a subject of a later special report concerned specifically with Messoiaikh and Vilyui deposits.

The number of publications authored by various scientists (Figure 2) is noteworthy. In spite of a great many publications covering a broad range of interrelated topics, significant repetition of materials is certainly one of the features of many papers. In this context, Makogon's book entitled **Hydrates of Natural Gas** (1974) is the best reference in the entire Russian literature on the gas hydrates field.

The possibility of widespread gas hydrate occurrence in offshore areas was presented by Cherskii at the 11th International Gas Congress in Moscow in 1970. Then, in subsequent years a few papers on gas hydrates in marine environments were published (Cherskii et al., 1972, 1977; Makogon, 1973; Trofimuk et al., 1975). The same and other authors have presented their projections on marine hydrates, which were mostly based on hydrate formation favorability with respect to temperature and pressure. While there is a lack in Russian literature of the pertinent data from seismic surveys, drilling, coring, pore fluid chemistry, etc., the potential offshore hydrate occurrence areas of the Soviet Union, the Russian projections on the marine hydrates have more conjectural than documented character.

From 1972 to 1976 the number of Russian publications on hydrates declined (Figures 1 and 2). This was probably due to diminished interest combined with lack of new data from the field and laboratories. However, at the same time (i.e. 1974) the most important book, Makogon's **Hydrates of Natural Gas** was published. In the late 1970s and 1980s in the USA and Canada, strong efforts were made toward a better understanding of the genesis and mechanisms controlling gas hydrate occurrences and developing the most applicable exploration methods. A number of special projects have been carried out by the Deep Sea Drilling Project (DSDP) and by the DOE - METC Gas Hydrates Program.

In the meantime Yefremova and Zhizhchenko (1972), Makogon (1974), and Cherskii and Tsarev (1977) hinted about the recovery of hydrates from the interval of 6.40 - 8.10 m below the Black Sea floor at station No. 116 from a water depth of 1,950 m.

During the period 1978 - 1982 the number of Russian publications shows an increase (Figure 1), which probably indicates rejuvenation of the interest in the subject matter in the Soviet Union. The bulk of the publications pertains to the prevention of gas hydrates in the pipelines (Byk and Fomina, 1981). With regard to the formation of hydrate deposits in natural environments, no significant new developments can be noted.

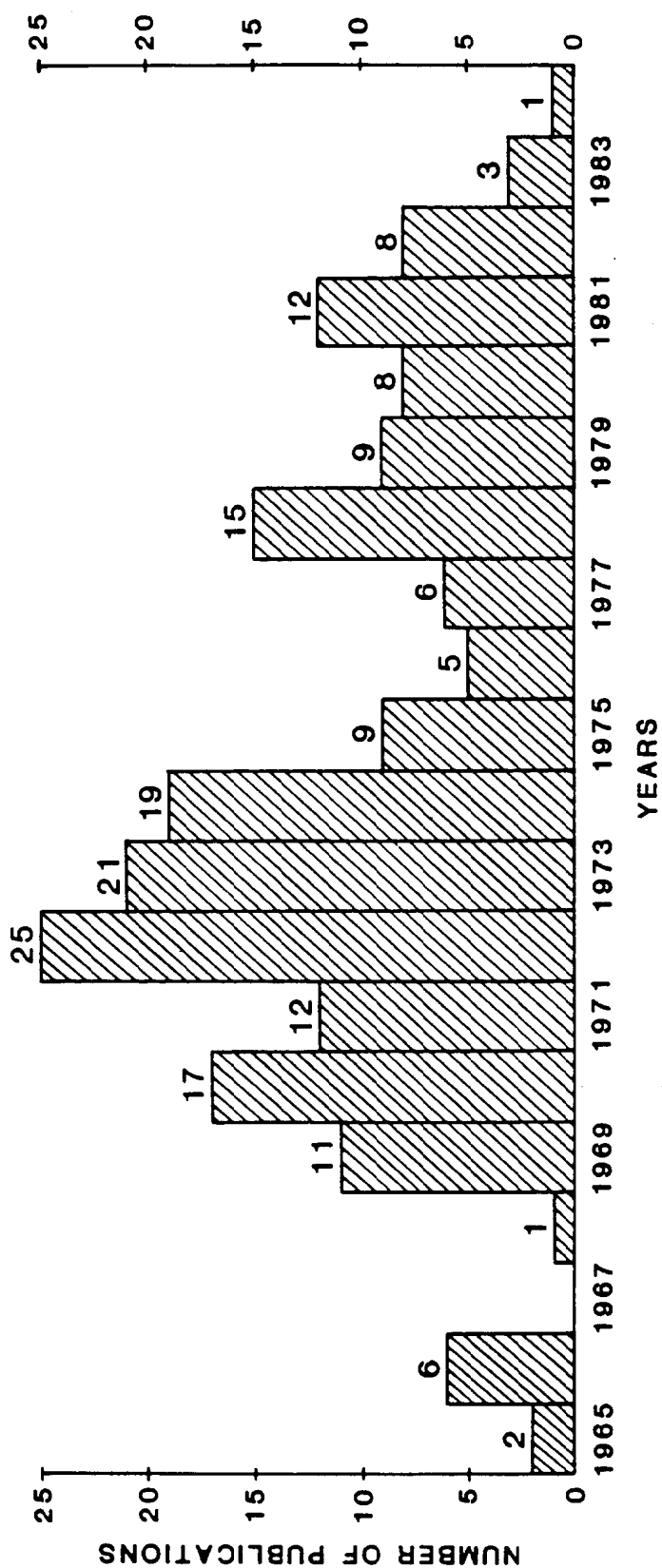
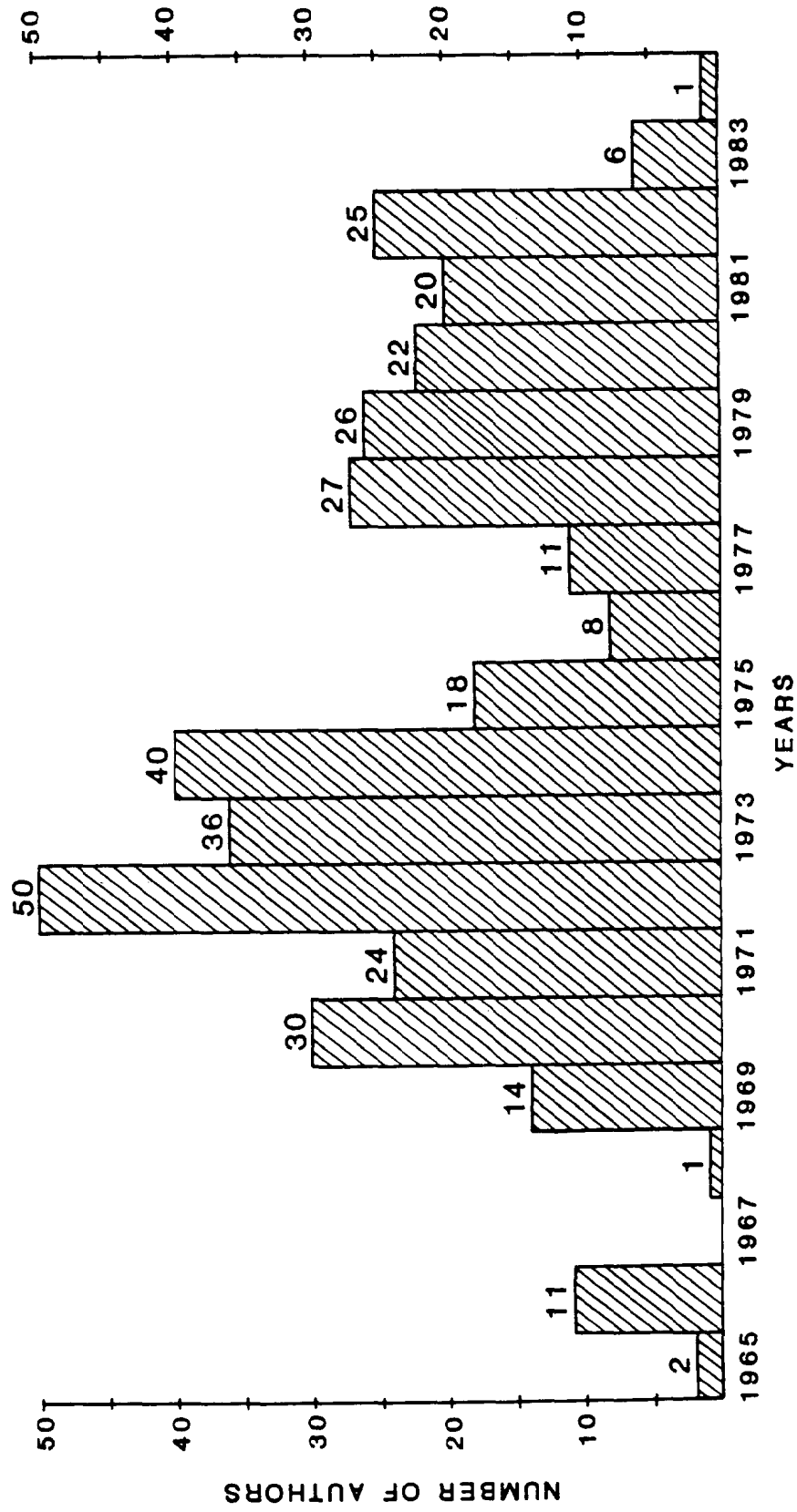


Figure 1. PUBLICATIONS RELEVANT TO THE GAS HYDRATES DEPOSITS  
PUBLISHED IN THE SOVIET UNION  
(1964 THROUGH 1984)

Note: Publications reviewed and considered for this report



**Figure 2. RUSSIAN AUTHORS' PUBLICATIONS RELATED TO GAS HYDRATES DEPOSITS  
(1965 THROUGH 1984)**

**Note:** Publications reviewed and considered for this report

## STRUCTURAL FEATURES OF GAS HYDRATES

In the Soviet Union, B.A. Nikitin (1939) was the first to point out that gas hydrates can occur in a solid form. Russian scientists (Byk, 1980) emphasize that that Nikitin's idea was further confirmed by German and American authors (von Stackelberg, 1954; Müller, 1954; Meinhold, 1954; van der Waals, 1959; and others). The latter group of scientists proved that gas hydrates constitute non-stoichiometric compounds of gas (or mixture of various gases) of a clathrate type. In such clathrates, the host lattice is made of hydrogen bonded water molecules. Gas molecules are held in crystallographic voids by van der Waals forces.

It appears that the Russian contribution in the field of structural research of gas hydrates has been rather marginal. Makogon (1974, 1980), Byk (1980) and Fomina (1980) do not cite any Russian names or major developments from the area of the gas hydrate structural investigation.

Thus, the fundamental discoveries of the crystallographic features of the gas hydrates were made in the early 1950s by Claussen (1957), Pauling, Marsch (1952), Müller and von Stackelberg (1952) who extensively used X-ray and mass spectrometry methods. These studies revealed that all known gas hydrates crystallize in one of two types of structures: Type I and Type II. The common unit in both structures is a pentagonal dodecahedron composed of water molecules.

In the Type I structure two pentagonal dodecahedra are packed in a body centered cubic array with polyhedra with twelve pentagonal and four hexagonal faces.

In the Type II structure 16 pentagonal dodecahedra are packed with six polyhedra with twelve pentagonal and two hexagonal faces. Sizes of the unit cells are 12 Å and 17.4 Å respectively for Types I and II (Figure 3). The Type I unit cell contains 46 water molecules, two small (dodecahedra) and six large (tetradecahedra) voids. The average diameter of a small void is 5.2 Å and 5.9 Å for the large void. Unit cell of Type II consists of 136 water molecules with 16 small voids (about 4.8 Å in diameter and 8 large voids (about 6.9 Å in diameter).

The sizes of voids and available gas molecules determine the type of hydrate structure, which will be stabilized. Gas molecules of the diameter ( $\emptyset$ ) bigger than 6.9 Å cannot form hydrates. If  $\emptyset$  of these molecules is smaller, the hydrate of Type I may form. When the size ( $\emptyset$ ) of a gas molecule is between 5.2 Å and 5.9 Å (e.g.  $\text{Br}_2$ ,  $\text{CH}_3\text{SH}$ ) then only large voids of the hydrate cell are filled with it. In this case, when all six large voids are filled up, its chemical formula will be  $M \times 7.66 \text{ H}_2\text{O}$ , where M stands for gas molecule. If the diameter of a gas molecule is smaller than 5.2 Å all voids of the cell may be filled with it and subsequently the formula of this hydrate will be  $M \times 5.75 \text{ H}_2\text{O}$ . This kind of hydrate can be formed from gases like Ar,  $\text{CH}_4$ ,  $\text{H}_2\text{S}$  (Figure 3A).

Hydrates of Type II structures may only form in the presence of large molecules with diameter ( $\emptyset$ ) which is between 5.9 Å and 6.9 Å (e.g.  $\text{C}_3\text{H}_8$ ,  $\text{iC}_4\text{H}_{10}$ ,  $\text{C}_3\text{H}_6$ ,  $\text{CHCl}_3$ , Figure 3A).

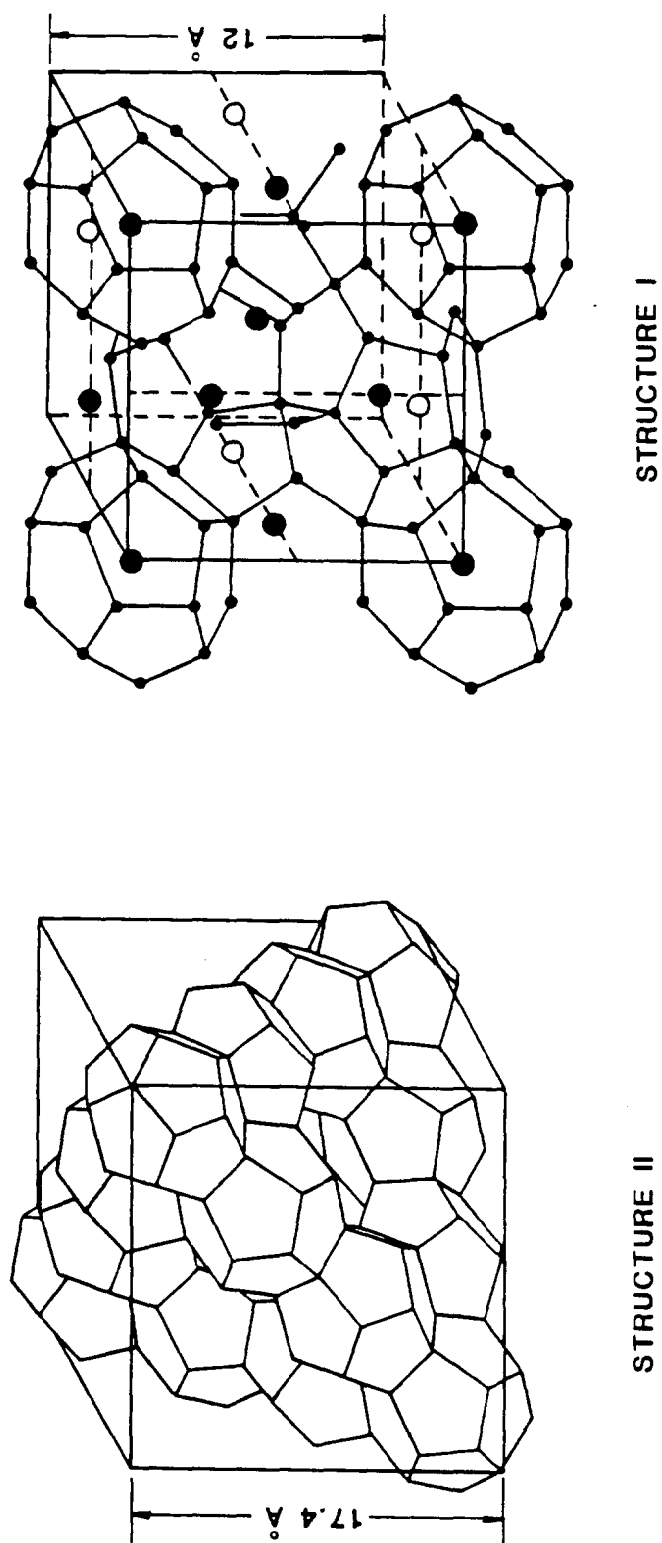
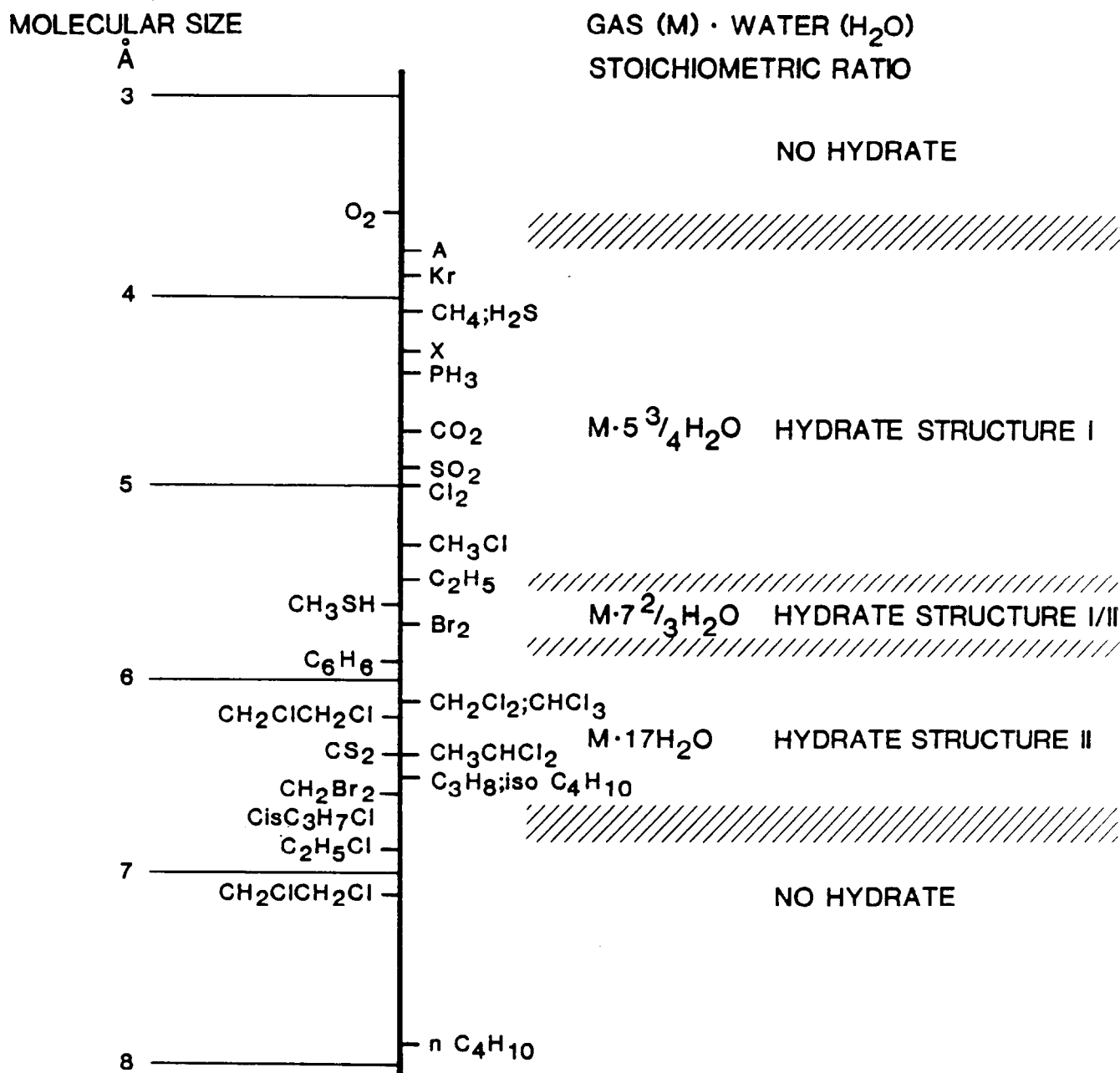


Figure 3. LATTICE STRUCTURES OF GAS HYDRATES

From Byk and Fomina (1966),  
after von Stackelberg and Müller (1954)



**Figure 3A. NOMOGRAM SHOWING THE SIZE OF GAS HYDRATE-FORMING MOLECULES**

From Makogon and Sarkis'yants (1966),  
after Hand et al. (1971)

If at the same time gas molecules with  $\bar{O} < 4.8 \text{ \AA}$  are available 16 small voids of the cell will be filled and the chemical formula of that mixed gas hydrate of Type II will be  $M \times 5.67 \text{ H}_2\text{O}$ .

Since the discoveries of Claussen, Pauling and the others, more advanced techniques - e.g. nuclear magnetic resonance and modernized mass-spectrometry - have been applied in the research of hydrates of various gases in western countries. However, with regard to the hydrates of hydrocarbon gases, the findings of the above mentioned Western scientists are extensively used also in the Soviet Union (Makogon, 1974; Byk, Makogon, Fomina, 1980).

## HYDROCARBON GENERATION AND GAS SOLUBILITY

Among the conditions affecting gas hydrate formation, hydrocarbon generation, gas solubility and specific thermodynamic conditions are of major importance. In this chapter, special attention is focused on hydrocarbon generation and gas solubility as discussed in the Soviet literature relevant to gas hydrates.

### Hydrocarbon Generation

Russian authors such as Trofimuk (1973, 1975), Cherskii (1973, 1975, 1977), Tsarev (1973, 1975, 1977), and Zorkin (1972) favor biogenic origin for marine gas hydrate deposits. Such opinion has been confirmed by isotopic analysis of  $\delta^{13}\text{C}$  from methane and carbon dioxide (Gutsalo, Plotnikov, 1981) on hydrocarbon gas concentrations in sea water and in the sediments.

The most comprehensive model of hydrocarbon generation related to gas hydrate formation in the marine environment, in Russian literature was given by Cherskii and Tsarev (1977). The summary of this model is shown in Figure 4. Cherskii and Tsarev demonstrated that natural gases do not buoyantly disperse and can be included within gas hydrates and remain physically bound within the sediment. After the sediment reaches the lower boundary of the gas hydrate stability zone, which moves upward with burial, the hydrates in the unstable zone dissociate. The gas liberated during the hydrate decomposition migrates upward to the hydrate stability zone. This explains higher concentration of gas in the bottom section of the hydrate zone (Cherskii et al., 1976).

It has been widely accepted that methane generation occurs in the areas of low oxidation potential (Eh), which may be close to the value at which hydrogen is liberated from water. That value of Eh was calculated by Zhilina and Zavarzin (1973) with a modified Nernst equation:

$$Eh = 0.168 - 0.0591 \text{ pH}$$

In accordance with Cherskii's and Tsarev's model (Figure 4), methane is basically generated by two types of reactions:

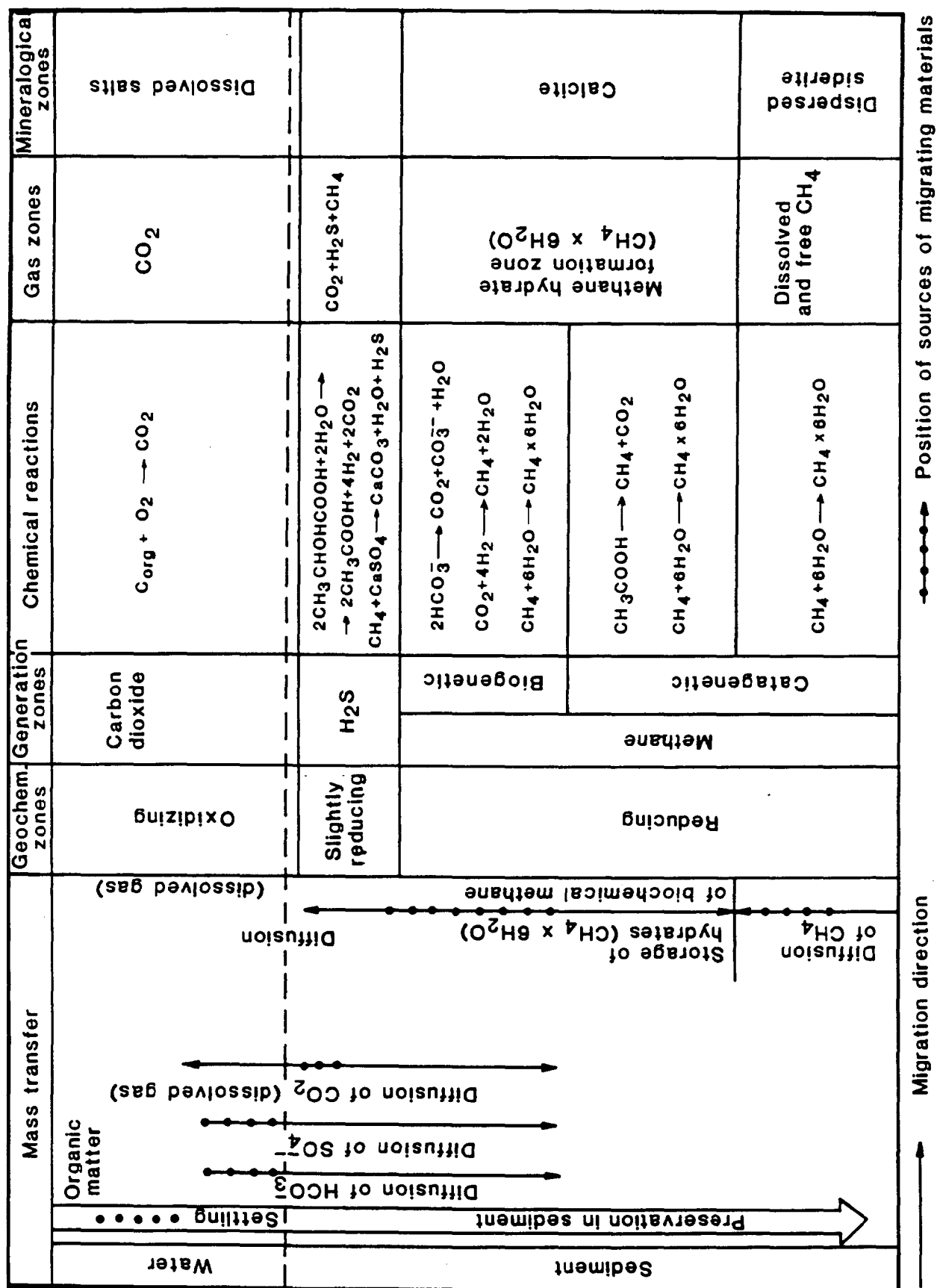


Figure 4. GENERATION AND ACCUMULATION OF BIOGENIC GASES IN HYDRATE-FORMATION ZONES OF OCEAN SEDIMENTS

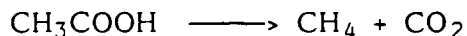
After Cherskii and Tsarev (1977)



1. reduction of  $\text{CO}_2$  in the process of bacterial sulfate consumption



2. breakdown of alcohol and low molecular weight acids, i.e.



The source of hydrogen in the first reaction can be organic matter and methane migrating upwards from its generation zone or molecular hydrogen formed during physico-chemical processes in sediments (Gusev et al., 1974). Cherskii and Tsarev do not, however, exclude the participation of mantle derived hydrogen in the process of  $\text{CO}_2$  reduction. The same authors point out that two zones can usually be distinguished in vertical profile of the sea floor sediment. The upper oxidation zone which ranges from several centimeters to several meters (composed of red clay). In the lower reduction zone, sulfates ( $\text{SO}_4^{2-}$ ) are reduced to sulfides and in some instances to sulfur.

The continuity of the methane generation process can be maintained when there is a steady supply of  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ , from seawater, and  $\text{CO}_2$  (dissolved gas) from the uppermost sediment strata, where most of the organic matter is decomposed (Figure 4). At the same time, the biochemical processes of the source material in the oxidation zone must be quite intensive (Cherskii and Tsarev, 1977). The authors of the model state that the maximum concentrations of generated methane do not exceed  $0.75 - 1.5 \text{ cm}^3/\text{cm}^3$  of sediment. Carbon dioxide is generated in the oxidation zone (see Figure 4). It can be transferred into the hydrate zone when the pressure is about 12 atm. The corresponding value of gas saturation in water theoretically may equal 16 l/l. However, the Russian authors admit that even under conditions where large quantities of organic matter reach the sea bottom such high concentration of  $\text{CO}_2$  is unlikely.

According to Cherskii and Tsarev (1977) the thickness of the upper oxidation zone varies from several centimeters in interior seas to 50 - 100 centimeters in deep marine basins. In the sediments of central parts of oceans the oxidation zone may exceed 5 meters in thickness.

On the shelves and continental slopes the depth of the reduction zone where sulfates are being reduced to sulfides varies from 1.5 to 2.0 meters. One of the major requirements for hydrate formation, i.e. high concentration of methane in water, can be met in the methane generation zone (Figure 4). This zone is usually located at depths of several centimeters to several meters below the sea floor and may extend to tens or hundreds of meters subbottom.

At certain thermodynamic conditions the process of gas hydrate formation may start when saline water is sufficiently saturated with the hydrocarbon gas (Barkan and Voronov, 1982). Cherskii and Tsarev (1977) made an attempt to prove through their calculations that in most cases the above mentioned conditions necessary for gas hydrate formation are fulfilled. In order to assess the balance of generated and dispersed biogenic methane the following parameters had to be determined:

1. thickness of gas generation zones of  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  and  $\text{CH}_4$ ,
2. concentrations of initial and final products of the biochemical reactions,

3. diffusion coefficients of the gases,
4. values for  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{CO}_2$  fluxes into the methane generation zone,
5. values of methane flux out of the methanogenic zone.

Russian authors (Romankevich, 1974; Trofimuk, 1973; Tsarev, 1975 and others) commonly use the values of diffusion coefficients (D) for gases and ions in the seawater obtained by Horne (1972) in their calculations.

TABLE 1.

DIFFUSION COEFFICIENTS (D) FOR  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{SO}_4^{2-}$  IN SEAWATER AT 4°C AND 20°C. After Cherskii and Tsarev (1977)

Molecule, ion	D at 4°C, $\text{cm}^2/\text{s}$	D at 20°C, $\text{cm}^2/\text{s}$
$\text{CH}_4$	$0.8 \times 10^{-5}$	$1.5 \times 10^{-5}$
$\text{CO}_2$	$1.2 \times 10^{-5}$	$2.0 \times 10^{-5}$
$\text{SO}_4^{2-}$	$0.7 \times 10^{-5}$	$0.9 \times 10^{-5}$

Diffusion coefficients (D) for  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{SO}_4^{2-}$  in uncompacted marine sediments (i.e. in the environment where the hydrates may be formed) adopted by Cherskii and Tsarev were previously determined by the American researchers Reed and Sherwood (1971) and Russian investigator Shishkina (1972). The latter scientists found the values of the coefficient D in marine sediments to be one third of those in seawater. Cherskii and Tsarev used the same value of D for  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  ions. The effect of ionic strength of water on gas diffusion was neglected in the study. Methane concentrations found in equilibrium with hydrates at various temperatures of water and sediment with porosity of 50% are shown on Table 2.

TABLE 2.

METHANE CONCENTRATIONS IN EQUILIBRIUM WITH HYDRATES AT VARIOUS WATER TEMPERATURES USED IN SEDIMENT WITH 50% POROSITY. After Cherskii and Tsarev (1977).

Temperature °C	Equilibrium pressure of methane over hydrates atm	Concentration of $\text{CH}_4$ dissolved in saline water, 35 g/l @ equilibrium pressure mole/ $\text{cm}^3$	$\text{CH}_4$ Concentration in sediment with porosity of 50% mole/ $\text{cm}^3$
4	30	$0.03 \times 10^{-3}$	$0.015 \times 10^{-3}$
8	50	$0.04 \times 10^{-3}$	$0.02 \times 10^{-3}$

For calculating the amount of carbon dioxide formed on a sediment surface which consequently enters the methane generation zone and disperses into the water column (Figure 4), Cherskii and Tsarev applied the following equations:

$$Q_{CO_2}^{H_2O} + Q_{CO_2}^h = Q_{CO_2}$$

$$Q_{CO_2}^{H_2O} = D_{CO_2}^{H_2O} \times C_{CO_2} / h_{CO_2}^{H_2O}$$

$$Q_{CO_2}^h = D_{CO_2}^h \times D_{CO_2} / h^h$$

where:

$Q_{CO_2}^{H_2O}$  = flux of  $CO_2$  into the water column (i.e.  $CO_2$  dispersed)

$Q_{CO_2}^h$  = flux of  $CO_2$  into sediment (i.e. into methane generation zone)

$h^h$  = distance from  $CO_2$  generation zone to methane generation zone in sediment.

$C_{CO_2}$  = concentration of  $CO_2$  in the zone of its generation.

$D$  = coefficient of diffusion.

The concentrations of  $CO_2$ ,  $SO_4^{2-}$  and  $HCO_3^-$  in the methane generation zone were set equal to zero by the authors, based on the assumption that all incoming components are completely transformed. At the same time the concentration values for  $SO_4^{2-}$  and  $HCO_3^-$  in seawater of equal  $56 \times 10^{-6}$  and  $2.3 \times 10^{-6}$  mole/cm<sup>3</sup> were used after Horne (1972).

Determination of the amount of generated methane in three major marine morphological zones (i.e. shelf, continental slope, oceanic floor) was based on the assumption that 2 moles of  $SO_4^{2-}$  and 1 mole of  $CO_2$  are required for generation of 1 mole of  $CH_4$  (Claypool et al., 1973). Values of  $SO_4^{2-}$ ,  $HCO_3^-$ ,  $CO_2$  fluxes into the methane generation zone used by Cherskii and Tsarev are shown in Tables 3 and 4.

These Russian authors estimated the amounts of methane dispersed from the generation zone in the presence of gas hydrates in the sediments. The results of this work are shown in Table 5.

Analysis of the presented data led Cherskii and Tsarev (1977) to the following conclusions:

1. Methane accumulation in shelf areas takes place where the depth of its generation is 0.5 m or more and the carbon dioxide flow front reaches the depth 5 m or more.
2. In the areas of continental slopes, these depths are 2 and 5 m.
3. For the oceanic floor the figures are > 10 m and > 10 m (i.e. depth of  $CH_4$  generation zone and  $CO_2$  flow front).

TABLE 3.

AMOUNT OF  $\text{SO}_4^{2-}$  AND  $\text{HCO}_3^-$  ENTERING METHANE GENERATION ZONE  
After Cherskii and Tsarev (1977).

Structural zone	Mean temperature °C	Coefficient of diffusion in sediment $\text{cm}^2/\text{s}$	$\frac{\text{SO}_4^{2-}}{\text{HCO}_3^-}$ concentration on sediment surface mole/cm	Amount of $\text{SO}_4^{2-}$ and $\text{HCO}_3^-$ entering the methane generation zone ( $\frac{\text{SO}_4^{2-}}{\text{HCO}_3^-}$ ) $\times 10^{11} \text{ mole cm}^{-2} \text{ s}^{-1}$			
				Depth zones (cm)			
				$0.5 \times 10^2$	$2 \times 10^2$	$5 \times 10^2$	$10 \times 10^2$ $15 \times 10^2$
Shelf	8	$0.25 \times 10^{-5}$	$\frac{0.056 \times 10^{-3}}{0.002 \times 10}$	$\frac{0.28}{0.01}$	$\frac{0.07}{0.005}$	$\frac{0.028}{0.001}$	$\frac{0.014}{0.0005}$ $\frac{0.009}{0.0003}$
Continental slope	4	$0.20 \times 10^{-5}$	$\frac{0.056 \times 10^{-3}}{0.002 \times 10}$	$\frac{0.22}{0.008}$	$\frac{0.086}{0.002}$	$\frac{0.022}{0.0008}$	$\frac{0.011}{0.0004}$ $\frac{0.007}{0.0002}$
Ocean floor	4	$0.20 \times 10^{-5}$	$\frac{0.056 \times 10^{-3}}{0.002 \times 10}$	$\frac{0.22}{0.008}$	$\frac{0.056}{0.002}$	$\frac{0.022}{0.0008}$	$\frac{0.011}{0.0004}$ $\frac{0.007}{0.0002}$



TABLE 5.  
AMOUNT OF CH<sub>4</sub> DISPERSING FROM ITS GENERATION ZONE.  
After Cherskii and Tsarev (1977).

Structural zone	Mean temperature °C	CH <sub>4</sub> diffusion coefficient (D) in sediment cm <sup>2</sup> ·s <sup>-1</sup>	Gas concentr. on the sediment surface mole·cm <sup>-2</sup>	Depth of Dispersing CH <sub>4</sub> x 10 <sup>11</sup> mole·cm <sup>-2</sup> ·s <sup>-1</sup>			
				Depth of CH <sub>4</sub> generation zone, cm			
				0.5x10 <sup>2</sup>	2x10 <sup>2</sup>	5x10 <sup>2</sup>	10x10 <sup>2</sup> 15x10 <sup>2</sup>
Shelf	8	0.30 x 10 <sup>-5</sup>	0.020 x 10 <sup>-3</sup>	0.12	0.03	0.012	0.006 0.004
Continental slope	4	0.25 x 10 <sup>-5</sup>	0.015 x 10 <sup>-3</sup>	0.075	0.019	0.0075	0.0037 0.0025
Ocean floor	4	0.25 x 10 <sup>-5</sup>	0.015 x 10 <sup>-3</sup>	0.075	0.019	0.0075	0.0037 0.0025

4. The amount of generated biochemical methane exceeds the amount of dispersing  $\text{CH}_4$  in most marine zones. Net average differences in the balance are equal  $0.07 \times 10^{-11}$ ,  $0.01 \times 10^{-11}$  and  $0.001 \times 10^{-11}$  mole/cm<sup>2</sup> x s) for continental shelf, continental slope, and ocean floor respectively.

Under the thermodynamically favorable conditions water saturated in methane is transformed into the gas hydrate. When 70 - 80% of the sediment is filled by the hydrates, the formation as a whole becomes a seal under which generated gas can accumulate in free state (Cherskii and Tsarev, 1977).

### Solubility of Gas in Water

Saturation of water with gases is one of the major factors in the process of gas hydrate formation. More precisely the problem should be formulated in two separate subject groups:

1. the solubility of the hydrocarbon gas in water under various pressure - temperature (P-T) conditions,
2. the relationship between P-T conditions and gas saturation in the process of gas hydrate formation.

In the collated Russian literature the most extensive discussion on gas solubility in water with respect to the gas hydrates was given by Makogon (1974).

In the Soviet Union, the scientific effort has been almost entirely directed to the acute problems of hydrate formation in gas pipelines in some northern areas of the country. So, the problem was addressed as water content in gases under various thermodynamic conditions. A number of experimental and analytical methods were developed in this area. Among the most commonly used methods Makogon (1974) cites:

1. visual determination of dew point; i.e. the temperature at which vapor condensation at a given pressure begins (the accuracy of this method is  $0.1^\circ\text{C}$ ),
2. use of solid adsorbing substances,
3. use of liquid adsorbing substances and their subsequent titration (water content of natural gases can be found with an accuracy of  $0.01 \text{ g/cm}^3$ ),
4. freezing out method,
5. spectroscopic methods, and
6. electro-hygrometric methods.

Another method of determining water vapor content in natural gases in standard conditions, suggested in the Russian literature (Makogon and Sarkis'yants, 1966) is using the nomogram shown on Figure 5. The nomogram is based on the work of Dodson and Standing (1944), McCarthy et al. (1950), Skinner (1948), Deaton and Frost (1938), Hammerschmidt (1933), and Brickell (1952). The error for this method does not exceed 4%. Generally the water content in natural gas increases with rising temperature and decreases with increasing pressure. An increase of water salinity (s) and molecular weight (f) of the gas further limit the amount of water vapor in gas. The two correction factors can be determined from the auxiliary charts on Figure 5. Makogon and Sarkis'yants (1966) recommend Bukacek's method as most useful for analysis and calculating the amount of water in natural gases. The method can be used over a wide range of pressure (1 to 700 kgf/cm<sup>2</sup>) and temperature (-40 to 230°C) where the following formula is applied:

$$W = \frac{A_t}{p} + B_t$$

where:

- W = water content in gas, g/cm
- A<sub>t</sub> = coefficient equal to the water content of an ideal gas, Table 6
- B<sub>t</sub> = coefficient dependent on gas composition, Table 6
- p = gas pressure (kgf/cm<sup>2</sup>)

Bukacek's formula is valid for natural gases with a gravity (Δ) equal to 0.6 in contact with fresh water (C<sub>s</sub> = 1). For the water vapor content in gases of different density in contact<sup>s</sup> with saline water the formula must be modified to:

$$W = \left( \frac{A_t}{p} + B_t \right) C_s C$$

where:

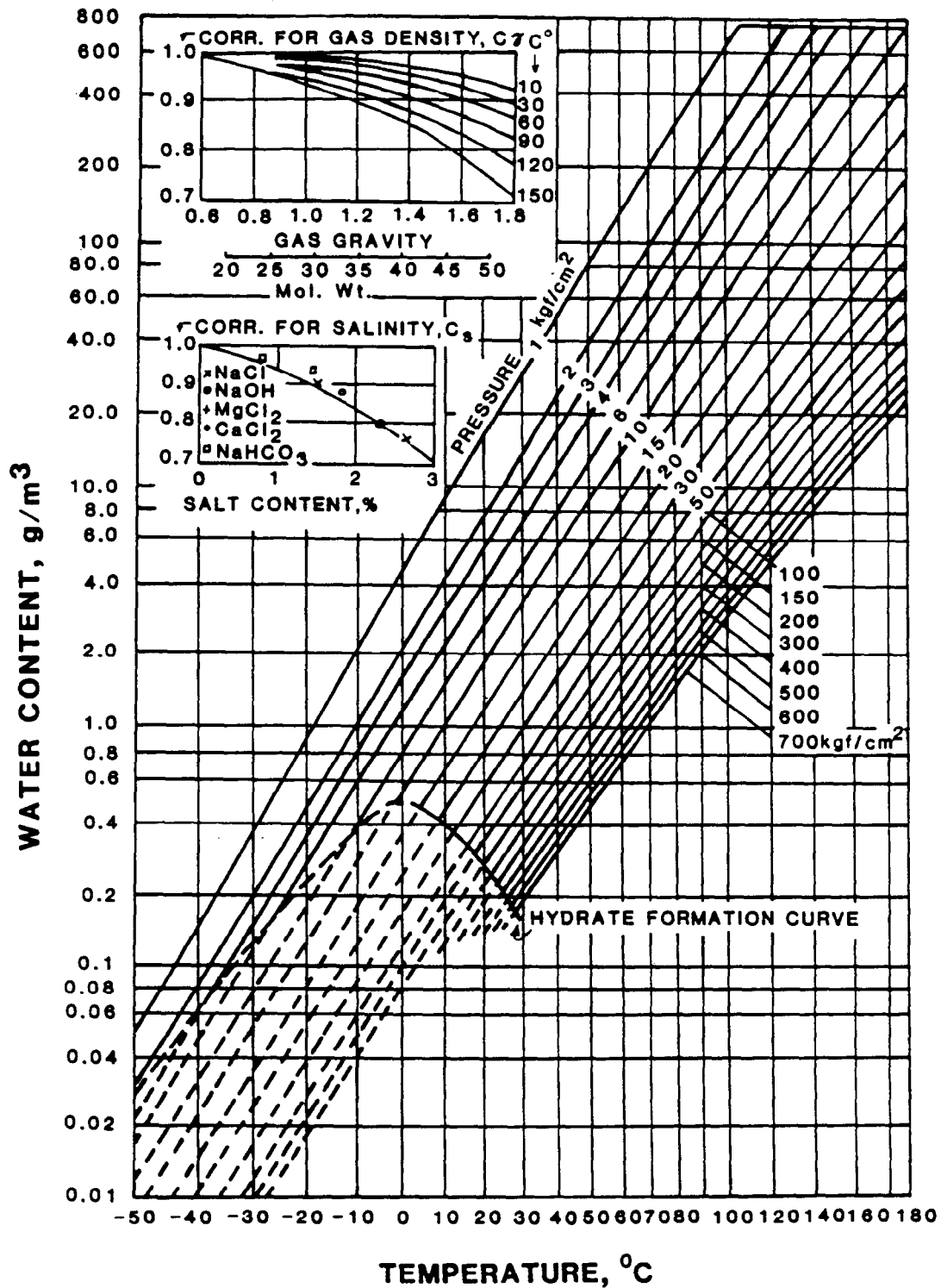
- C<sub>s</sub>, C = correction factors for water salinity and gas density

In the process of gas hydrate formation, solubility of the gas in the liquid phase is of prime importance. Hydrocarbon gas solubilities at temperatures above 20°C had been studied extensively in the Soviet Union prior to 1974 (Makogon and Koblova, 1971; Tsarev, 1971; and Cherskii, 1971). It was found that natural gases can be dissolved relatively easily in water even at low pressures. The solubility diminishes with an increased molecular weight of hydrocarbons. Also, Russian investigators discovered that the presence of carbon dioxide and hydrogen sulfide increases the solubility of hydrocarbon gases in water, while nitrogen, hydrogen, and helium diminishes the solubility of hydrocarbons (Trofimuk et al., 1980).

For calculating the content of dissolved water in hydrocarbon gas Makogon (1974) used the following formula:

$$RT \ln \frac{f_i}{N_i} = RT \ln k_i + \bar{V}_i (P - P_i)$$





**Figure 5. NOMOGRAM FOR THE DETERMINATION OF THE WATER CONTENT OF NATURAL GASES**

From Makogon and Sarkis'yants (1966),  
after McCarthy et al. (1950)

TABLE 6.

COEFFICIENTS  $A_t$  AND  $B_t$  FOR CALCULATION OF WATER CONTENT IN GAS  
BY BUKACEK'S METHOD. After Makogon and Sarkis'yants (1966).

Temperature °C	$A_t$	$B_t$	Temperature °C	$A_t$	$B_t$
-40	0.1451	0.00347	+32	36.10	0.1895
-38	0.1780	0.00402	+34	40.50	0.207
-36	0.2189	0.00465	+36	45.20	0.224
-34	0.2670	0.00538	+38	50.80	0.242
-32	0.3235	0.00623	+40	56.25	0.263
-30	0.3930	0.00710	+42	62.70	0.285
-28	0.4715	0.00806	+44	69.25	0.310
-26	0.5660	0.00921	+46	76.70	0.335
-24	0.6775	0.01043	+48	85.29	0.363
-22	0.8090	0.01168	+50	94.00	0.391
-20	0.9600	0.01340	+52	103.00	0.422
-18	1.1440	0.01510	+54	114.00	0.454
-16	1.350	0.01705	+56	126.00	0.487
-14	1.590	0.01927	+58	138.00	0.521
-12	1.868	0.021155	+60	152.00	0.562
-10	2.188	0.02290	+62	166.50	0.599
- 8	2.550	0.0271	+64	183.30	0.645
- 6	2.990	0.3035	+66	200.50	0.691
- 4	3.480	0.03380	+68	219.00	0.741
- 2	4.030	0.03770	+70	238.50	0.793
- 0	4.670	0.04180	+72	260.00	0.841
+ 2	5.400	0.04640	+74	283.00	0.902
+ 4	6.225	0.0515	+76	306.00	0.965
+ 6	7.150	0.0571	+78	335.00	1.023
+ 8	8.200	0.0630	+80	363.00	1.083
+10	9.390	0.0696	+82	394.00	1.148
+12	10.720	0.767	+84	427.00	1.205
+14	12.390	0.0855	+86	462.00	1.250
+16	13.940	0.0930	+88	501.00	1.290
+18	15.760	0.1020	+90	537.50	1.327
+20	17.870	0.1120	+92	582.50	1.327
+22	20.150	0.1227	+94	624.00	1.405
+24	22.800	0.1343	+96	672.00	1.445
+26	25.500	0.1453	+98	725.00	1.487
+28	28.700	0.1595	+100	776.00	1.530
+30	32.300	0.1740	+110	1093.06	2.620

where:

- $f_i$  = fugacity of a gas in the gaseous phase
- $N_i$  = molar fraction of the gaseous component dissolved in the water (i.e. the ratio of number of moles of a component in solution and the total number of moles of water and all dissolved components).
- $k_i$  = Henry's coefficient
- $T_i$  = temperature, K
- $P$  = pressure, atm
- $P_i$  = solvent vapor pressure, atm
- $\underline{R}$  = gas constant
- $\underline{V}_i$  = partial molar volume of "i"th gas component in water

Development of the gas industry in northern regions of the Soviet Union necessitated further studies of gas solubility in water at temperatures below 20°C. This research was mainly performed in the late 1960s and early 1970s at Gublin Petrochemical and Gas Industry Institute in Moscow. The diagrams presented on Figures 6 and 7 were made and are based on the results of these investigations (Makogon and Koblova, 1972). Figure 6 shows methane solubility in water at 20°C, 14°C and 10°C in the pressure range 0 - 120 kgf/cm<sup>2</sup>. The diagram displays the increase of methane solubility with rising pressure. Under conditions of low pressure the gas solubility increases when the temperature of a solution is lowered. The maximum value of gas solubility in water at a given temperature corresponds to the equilibrium pressure of hydrate formation. The diagram in Figure 7 shows change in methane solubility in water as a function of pressure at 10°C. The maximum value of dissolved gas equal to 1.95 cm<sup>3</sup> per 1 g of water is attained at 76 kgf/cm<sup>2</sup>. Further pressure increase leads to sharp decrease of gas solubility. At the same time the value of pressure corresponds to the equilibrium conditions of gas hydrate formation (Makogon, 1971).

In the process of hydrate formation the gas content of water changes. According to Makogon (1974) these changes are determined mostly by the gas diffusion within the volume of liquid water or through the hydrate film. Makogon (1974) states that after a hydrate film is formed, the diffusion of gas molecules within the liquid phase (water) is faster than through the hydrate film. Concurrently, gas from the hydrate phase diffuses into the water, thus saturating it to the point of its equilibrium content. The equilibrium gas content in water in the presence of hydrates depends on the partial pressure of gas under the hydrate film, on the rate of gas diffusion through the hydrate film, and of the surface tension of the water-hydrate interface.

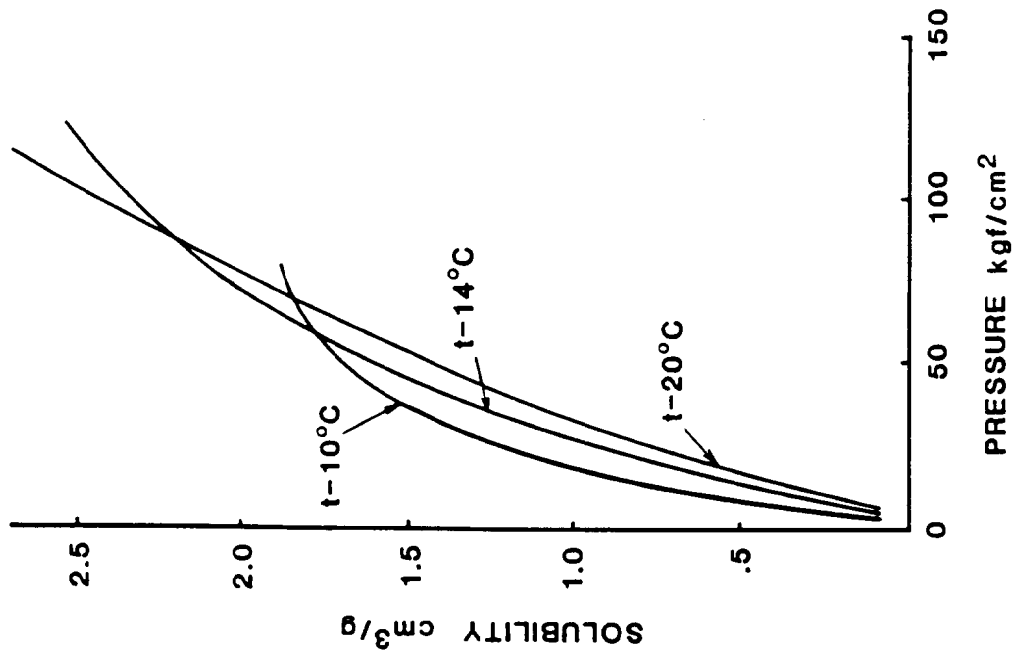


Figure 6. METHANE SOLUBILITY IN WATER  
After Makogon (1984)

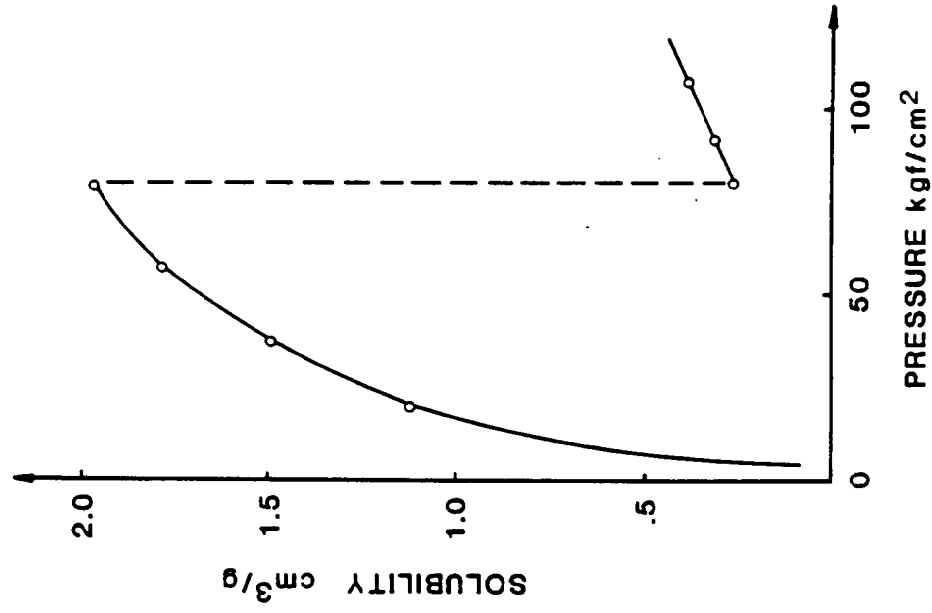


Figure 7. SOLUBILITY OF METHANE IN  
WATER AT 10°C  
After Makogon et al. (1971)

## THE FORMATION OF NATURAL GAS HYDRATES

### Kinetics of Gas Hydrate Formation

The phenomenon of gas hydrate formation is still poorly understood. Numerous investigations performed in the Soviet Union have shown that the process is not uniform (Makogon, 1974). Since 1964 a number of experiments on gas hydrate formation have been conducted at the Gubkin Petrochemical and Gas Industry Institute in Moscow. In the first group of experiments gas hydrates were formed in various temperature and pressure ranges on gas-water or gas-metal (experimental chamber) interfaces. These experimental settings related more to hydrate formation in pipelines, and furnished basic data concerning the mechanism of the process. After the discovery of natural gas hydrate deposits, laboratory experiments and theoretical studies were extended by introducing a porous medium as the environment of hydrate formation. The most complete results from these two groups of experiments have been described by Makogon (1974).

#### Natural Gas Hydrate Formation Under Conditions of Free Water-Gas Interface.

The experiments were conducted in hermetic analytical chamber over a wide range of temperature and pressure conditions using distilled water and two types of natural gas:

a - methane of 99.9% purity

b - gas composed of:  $\text{CH}_4$  - 92.14%;  $\text{C}_2\text{H}_6$  - 5.05%;  $\text{C}_3\text{H}_8$  - 1.27%;  $\text{iC}_4\text{H}_{10}$  - 0.14%;  $\text{nC}_4\text{H}_{10}$  - 0.1%;  $\text{N}_2$  - 1.3%.

The maximum operating pressure in this series of experiments was 200 kgf/cm<sup>2</sup> while the maximum temperature was 30°C. In order to eliminate the influence of heat of crystallization on the temperature at which the hydrate formed, the rate of cooling of the condensed water was not greater than 0.5°C per hour.

Researchers from the Gubkin Petrochemical and Gas Industry Institute had found that the process of gas hydrate formation begins with the appearance of hydrate nuclei at the gas-water contact. There were three possible kinds of contact in the experimental conditions:

- interface of water and gas phase (e.g. in a pipeline),
- surface of a gas bubble within water phase,
- surface of a water drop condensed on the wall of a chamber containing gas.

Formation of nuclei starts with the coalescence of individual clusters of water molecules. During the experiments temperature was found to be a major factor in determining the number and size of these clusters. In the process of cooling below the temperature of hydrate formation, the water is temporarily in a metastable condition (Figure 8). Once initiated, hydrate crystallization progresses actively. Further crystallization of hydrates is determined by thermal-pressure conditions and the rate of cooling (i.e. the rate at which the heat of hydrate crystallization is being "removed").

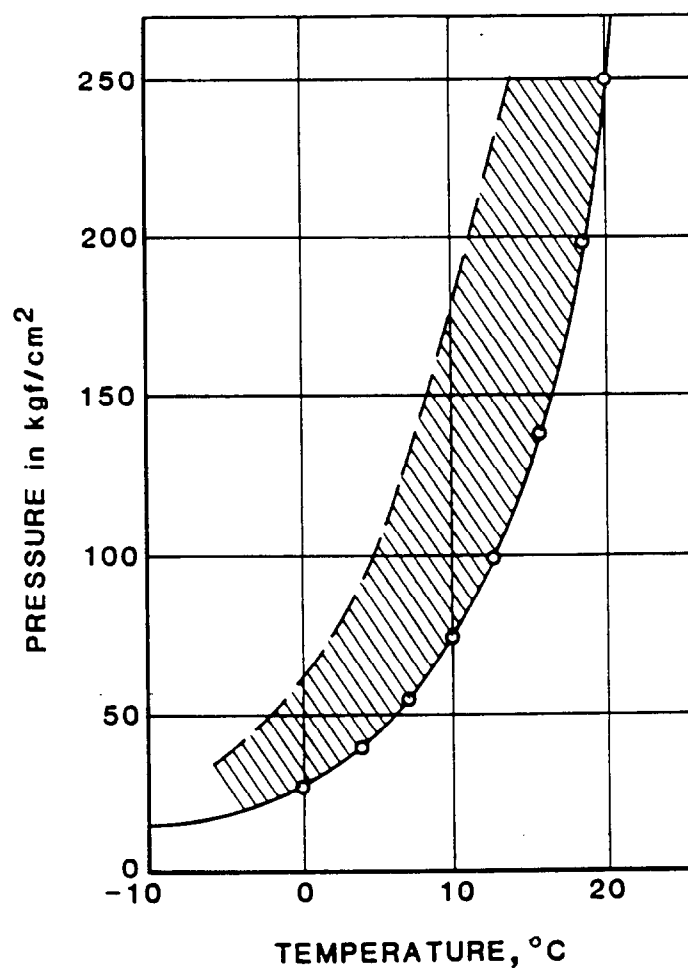
The relationship between thermodynamic conditions of hydrate formation and the presence of crystal nuclei was also studied in a series of experiments at Gubkin Petrochemical and Gas Industry Institute in Moscow (Makogon, 1974). Water from dissociated gas hydrates was preheated and then cooled gradually in various ranges of temperatures and pressures. Invariably, lower temperatures were required to reform hydrates following the heating of dissociation products to higher temperatures. Figure 9 illustrates the effect of heating water obtained from methane hydrate over various time ranges on hydrate formation. The upper and lower series of curves represent the pressure condition at 177 kgf/cm<sup>2</sup> and 75 kgf/cm<sup>2</sup> respectively. Comparison of the two sets of curves shows that in lower pressure conditions the effect of the water heating on the temperature of nucleation increases. Russian researchers observed a similar relationship in the case of ethane hydrate formation (Figure 10.) The maximum heating temperature which affects the P-T conditions of the hydrate crystallization was found to be 30 - 35°C. Heating the dissociated components above these temperatures does not have any effect on the initial conditions of gas hydrate formation. This phenomenon is explained by different values of chemical potential of water. Water obtained from the hydrate decomposition has greater chemical potential than freshly condensed water or water heated up to the temperatures above 35°C. Below 35°C the water preserves to a certain degree a crystalline hydrate structure. The greater the destruction of the relict hydrate structure, the greater is the supercooling required to form hydrates (Figure 11).

According to Makogon (1974) the process of hydrate crystallization starts by formation of particles which become centers (i.e. nuclei) of further hydrate development. There is a critical size of a gas hydrate nucleus necessary for its stabilization. This size depends on the crystallization heat, degree of supercooling and on specific surface energy. It can be expressed by this formula:

$$r_k = \frac{2\sigma T_p}{Q_r(T_p - T_o)} ,$$

where:

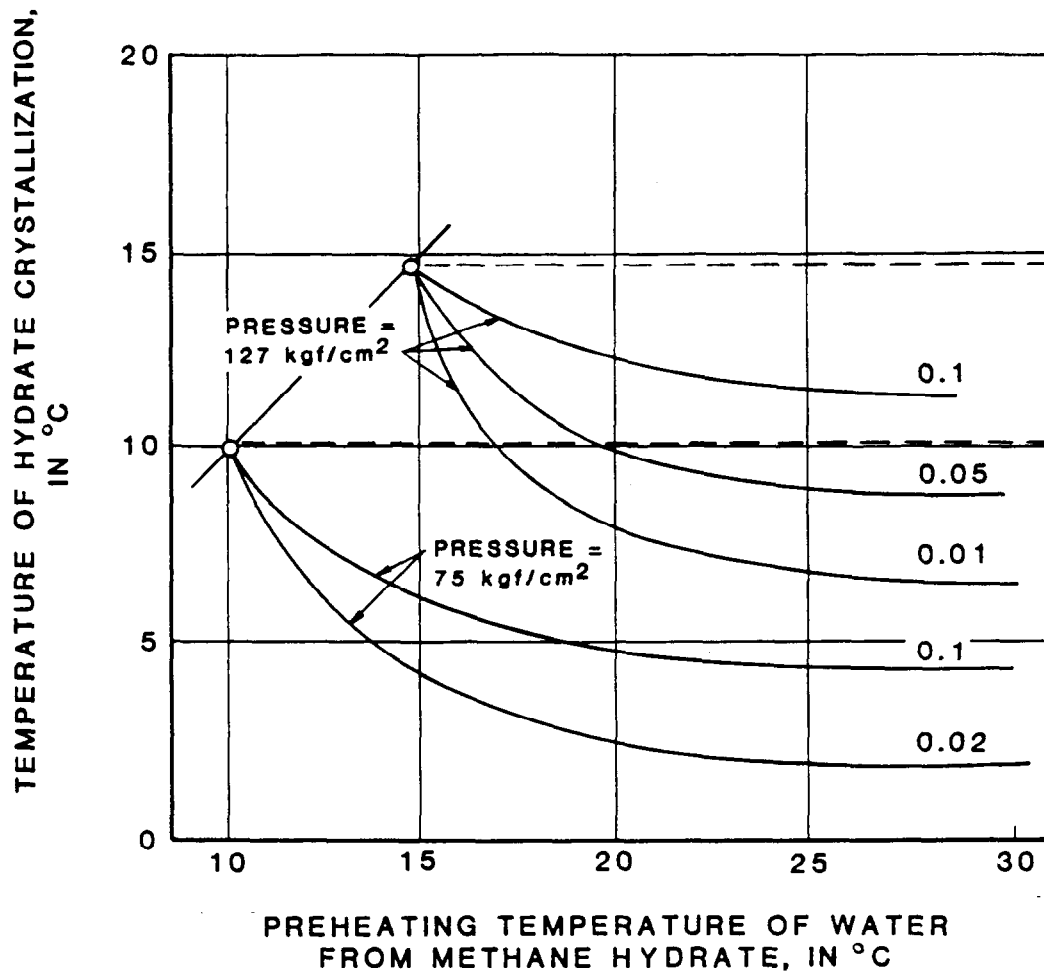
- $r_k$  = radius of the nuclei, Å
- $\sigma$  = specific nuclei surface energy, cal
- $Q_r$  = heat of crystallization, cal/mole
- $T_p$  = equilibrium temperature of crystallization, K
- $T_o$  = current temperature of crystallization, K



**Figure 8. AREA OF METASTABLE STATE OF WATER DURING METHANE HYDRATE CRYSTALLIZATION**

**After Makogon (1974)**

**Note:** Dashed curve represents conditions at which crystallization is initiated, solid curve represents conditions at which crystals dissociate. Hatched area is the region of metastable conditions.

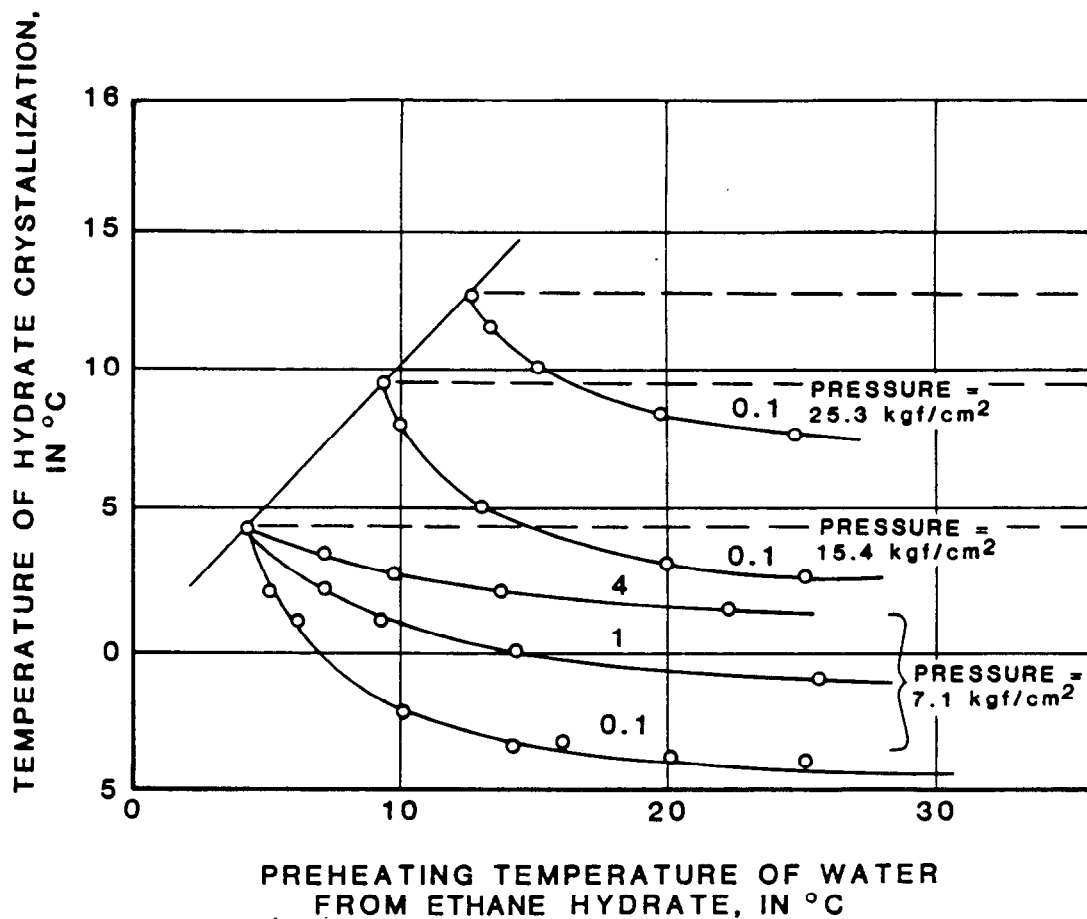


**Figure 9. RELATIONSHIP BETWEEN THE TEMPERATURE OF METHANE-HYDRATE WATER PREHEATING, AND THE TEMPERATURE OF THE HYDRATE CRYSTALLIZATION**

**After Makogon (1974)**

**Note:** Numbers on curves represent ratio of stabilization time of a newly formed hydrate to the time of holding the water at heating/temperature.

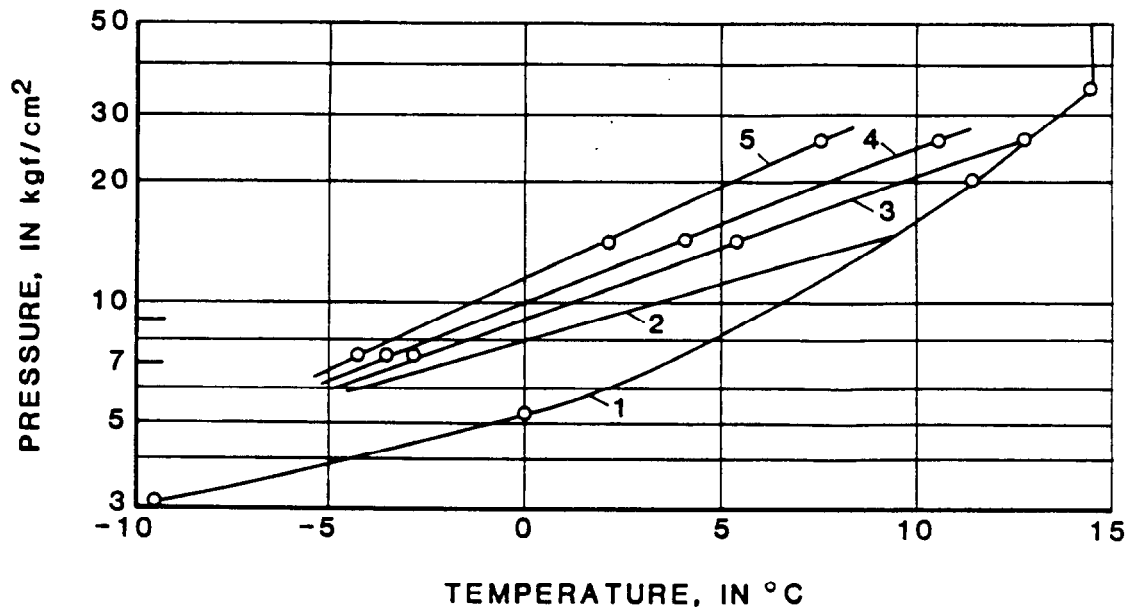




**Figure 10. RELATIONSHIP BETWEEN THE TEMPERATURE OF ETHANE-HYDRATE WATER PREHEATING, AND THE TEMPERATURE OF HYDRATE CRYSTALLIZATION**

**After Makogon (1974)**

Note: Numbers on curves represent ratio of stabilization time of a newly formed hydrate to the time of holding the water at heating/temperature.



- 1 - equilibrium curve for ethane hydrate formation,
- 2 - secondary gas hydrate formation from the water (obtained from dissociation of the hydrate) preheated to 9.5°C,
- 3 - secondary gas hydrate formation after the dissociation products were heated to the temperature of 12.8°C,
- 4,5 - secondary gas hydrate formation after the dissociation products were heated to 14°C and 30°C respectively.

**Figure 11. EQUILIBRIUM CURVES OF ETHANE HYDRATE FORMATION FROM PREHEATED WATER**

**After Makogon (1974)**

As long as the nuclei have not reached that critical size they remain instable and dissociate fairly easily. If the process of the crystallization continues, it involves the growth of hydrate around the nuclei. During the experiments performed at the Gubkin Petrochemical and Gas Industry Institute, the growth of hydrates at this stage progressed in three environments:

- a. on the gas-water interface (as surface film hydrate),
- b. in the gas volume (as volume diffusion hydrate), and
- c. within the water volume (as volume diffusion hydrate).

The rate of growth of the hydrate phase was found to be quite high. The experiments showed that under a pressure of  $5.5 \text{ kgf/cm}^2$  the growth rate can reach  $1 \times 10^{-4} \text{ A/sec}$ . The same experiments showed that gas hydrate crystallization is significantly controlled by gas diffusion rates to the hydrate growth site and by the amount of heat evolved during the process. Delivery of the hydrate forming gas to the growth site occurs by diffusion through the film of hydrate formed on the water-gas interface or by a gas stream containing water vapor with higher volatility than water vapor above the hydrate. The process of hydrate formation on the water-gas interface continues with the spreading of the hydrate film over the interfacial surface. The number of gas molecules in the water is greatest at the interface. Consequently, the surface layer of water is also supersaturated with gas. The rate of hydrate growth in lab conditions can be accelerated by pressure increase, a temperature decrease, or a decrease in relative gravity of the gas.

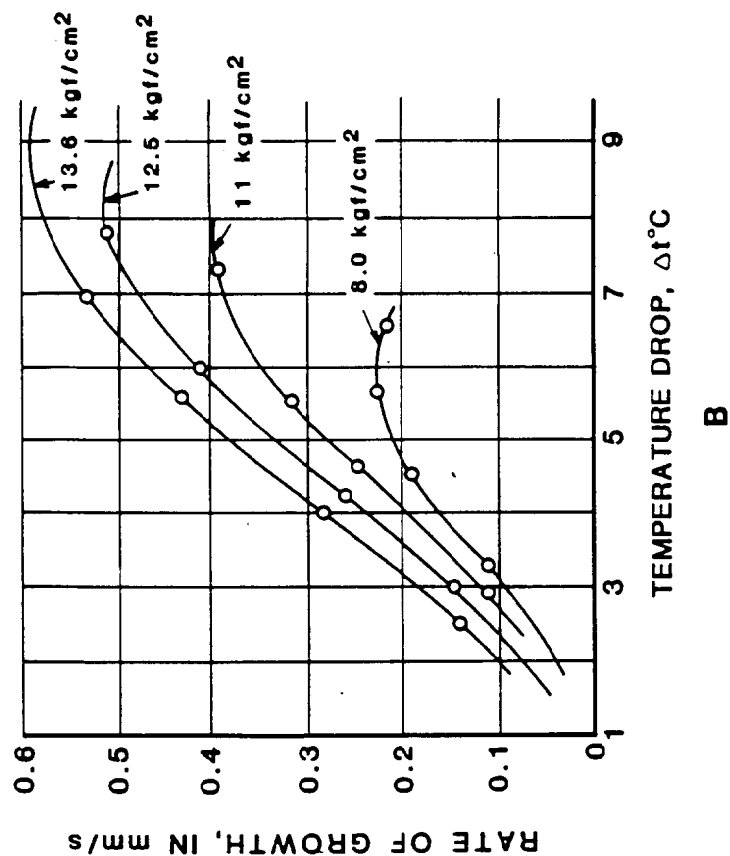
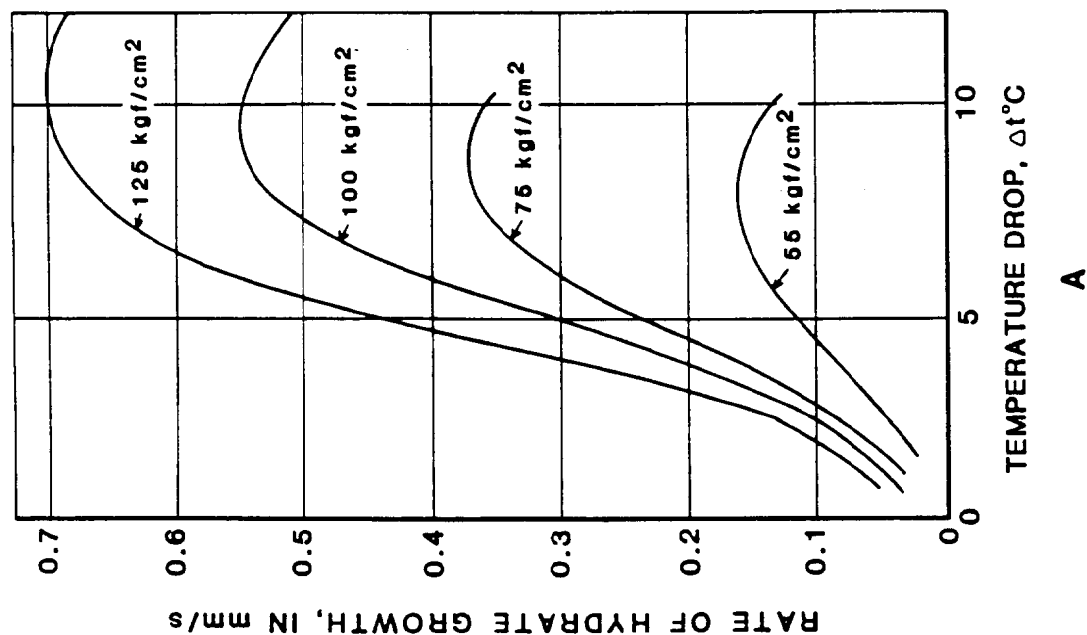
The Russian experiments showed that after the hydrate film has formed over the entire free gas-water interface, the process of hydrate growth changes from surface growth to volume diffusion type growth. This growth is relatively fast initially and then slows proportionally with increasing hydrate thickness (Figure 12).

In cases where water in liquid phase with dissolved gas is present over the crystallization nuclei, threadlike visceral hydrates usually develop (Makogon, 1974; Byk and Fomina, 1981). Visceral crystals are defined as crystals growing from the base. Such crystal growth may occur when gas is supplied to the base of already existing hydrate crystals. No relationship between the shape of visceral crystals and gas composition has been discovered. The crystals take the form of curved linear threads, needles and threadlike crystal colonies.

According to Makogon (1974), the mechanism of visceral growth has not yet been sufficiently explained neither theoretically nor experimentally. In his opinion the existing theories are often in contradiction with one another. In particular they fail to explain the conditions under which crystal growth on active surfaces starts and ceases.

### **Natural Gas Hydrate Formation in Porous Environments**

The mechanism of hydrate formation in a porous environment is of interest in view of the potential of hydrates as a resource of natural gas in the geological environment. First studies on natural gas hydrate formation in a porous medium, carried out at the Gubkin Petrochemical and Gas Industry Institute in Moscow revealed that lower temperatures and higher pressures are



**Figure 12. RATE OF RADIAL GROWTH OF METHANE (A) AND ETHANE (B) HYDRATES ON FREE GAS-WATER INTERFACE UNDER VARIOUS SUPERCOOLING AND PRESSURE CONDITIONS**

After Makogon (1974)

needed compared with a free gas-water contact. This is primarily due to changes in water vapor pressure (Makogon, 1974). Three types of water must be considered in a porous environment:

- a. free water which migrates under very small potential gradients and gravity,
- b. capillary water,
- c. bound water which forms adsorption films on the surfaces of the rock grains.

The reduction of vapor pressures of both bound and capillary water occurs as a result of variations of adsorption and surface tension forces. Change of water vapor pressure in porous environment can be mathematically expressed as follows (Makogon, 1974):

$$P = P_w - P_p$$

$$P_{pk} = P_w \left( 1 - \exp \frac{(P_w \cdot d)^2}{0.0126} \right)$$

Considering the second equation, the first expression can be rewritten as:

$$P = P_w - P_w \left( 1 - \exp \frac{(w \cdot d)^2}{0.0126} \right)$$

where:

$P$  = change of water vapor pressure in a porous environment, relative to free gas-water contact, kgf/cm<sup>2</sup>

$P_w$  = water vapor pressure above free gas-water surface, kgf/cm<sup>2</sup>

$P_p$  = water vapor pressure above the surface of bound water, kgf/cm<sup>2</sup>

$w$  = content of bound water in millimoles per 1 g of the adsorbent (rock)

$d$  = solid particle diameter, mm

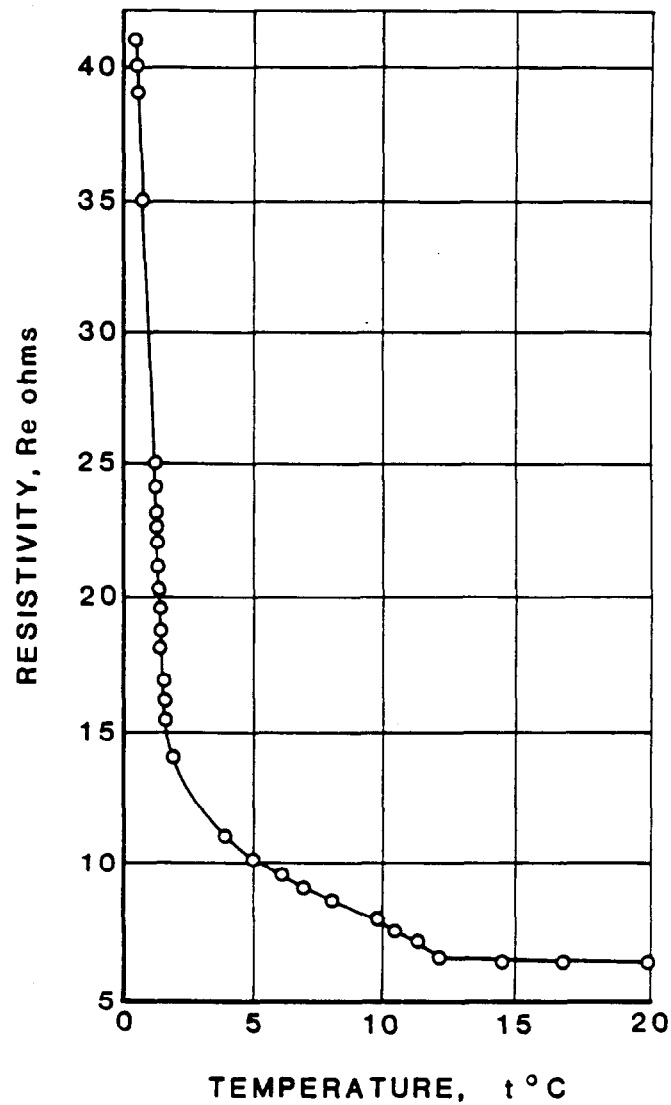
Thus, with smaller diameter rock grains (i.e. smaller capillary radius) the depression of water vapor pressure is greater and consequently a lower temperature is required for the initiation of hydrate formation in porous environments.

Experimental studies at the Gubkin Petrochemical and Gas Industry Institute were conducted using special apparatus with which conditions of hydrate formation could be strictly controlled. The start of hydrate formation can be easily detected from the curves of changing resistivity, temperature and pressure in the analytical chamber (Figures 13A and 13B).

Three sets of experiments in porous media described by Makogon (1974) elucidate basic physical relationships of hydrate formation. The laboratory conditions in the first series of experiments were as follows:

- volume of chamber,  $V_{ch} = 680 \text{ cm}^3$

- volume of pores,  $V_p = 238 \text{ cm}^3$



Specific resistivity ( $\varrho$ ) is calculated by:

$$\varrho = \frac{Re \times \pi \left(\frac{D}{2}\right)^2}{l}$$

where:

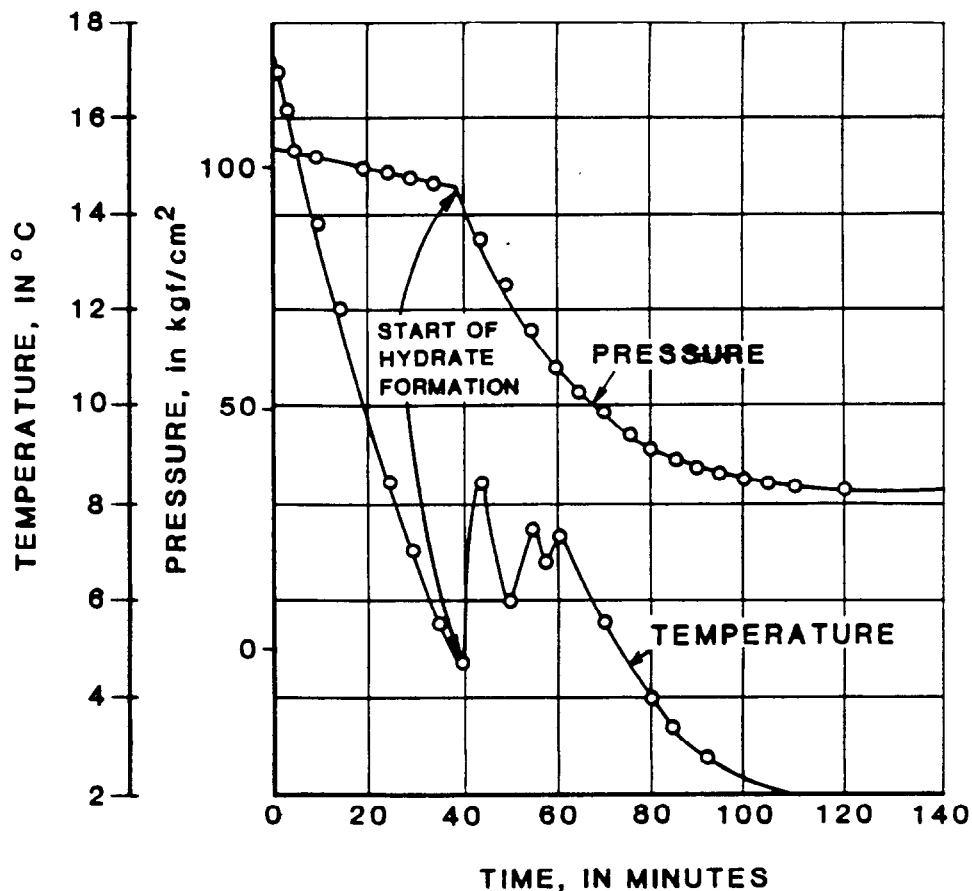
Re - resistivity (ohms)

D - diameter of core sample (meters)

l - length of a core sample (meters)

**Figure 13A. ELECTRICAL RESISTIVITY CHANGE IN POROUS MEDIUM DURING THE PROCESS OF GAS HYDRATE FORMATION**

**After Makogon (1974)**



**Figure 13B. EFFECT OF COOLING RATE  
ON THE TEMPERATURE AT WHICH  
GAS HYDRATE BEGINS TO FORM**

**After Makogon (1974)**

- porosity,  $\emptyset = 34.7\%$
- water saturation;  $S_w = 56\%$
- effective initial porosity,  $\emptyset_c = 15.6\%$
- effective capillary radius,  $r_e = 28 \times 10^{-4} \text{ cm}$
- initial pressure in chamber,  $P = 70 \text{ kgf/cm}^2$
- initial temperature in chamber,  $t = 20^\circ\text{C}$

The experiments were carried out in such a manner that the quantity of water and gas in the chamber were maintained constant while temperature and pressure were varied. After lowering the temperature, the pressure was stabilized to equilibrium conditions. The pressure in the experimental chamber was lowered to the point when all free water was converted into hydrates. After this point further lowering of temperature led to an insignificant drop of pressure, until 40 minutes into the experiment (Figure 15). At this time gas hydrates started to form. This event is marked by sharp increase of temperature in the chamber and lower equilibrium pressure.

The Russian experiments also showed that for multi-component gases, the temperatures of gas hydrate formation are lower. Makogon (1974) provides a twofold explanation to this fact:

1. Gas hydrate formation decreases the effective capillary radius and consequently diminishes water vapor pressure which is directly responsible for the depression of hydrate formation temperature.
2. During the process of gas hydrate formation the components with lower vapor pressure are the first to be converted into hydrates. The remaining free gas is then enriched in components which do not form hydrates easily (Figure 14). These latter components require significantly higher degree of cooling for their conversion into hydrates than the original gas mixture (Figure 15).

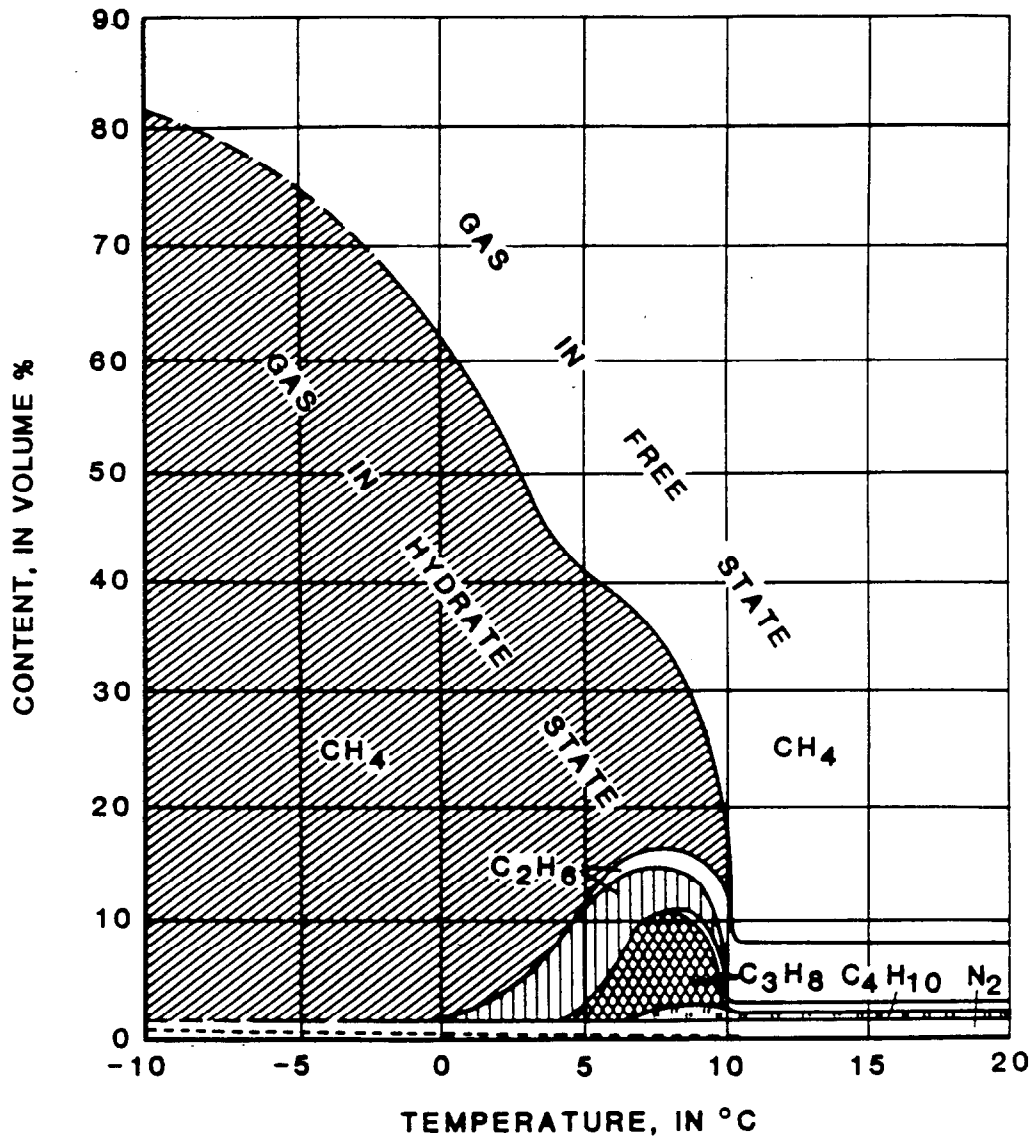
The nature of changes of various parameters during these experiments are shown in Table 7.

A second series of experiments had similar parameters as in the first one, except that initial pressure and temperature were  $232 \text{ kgf/cm}^2$  and  $27^\circ\text{C}$  respectively. The results are shown in Figure 16. In addition to the previously stated conclusions, it was found that in lower ranges of pressure the influence of the porous environment on gas hydrate formation increases.

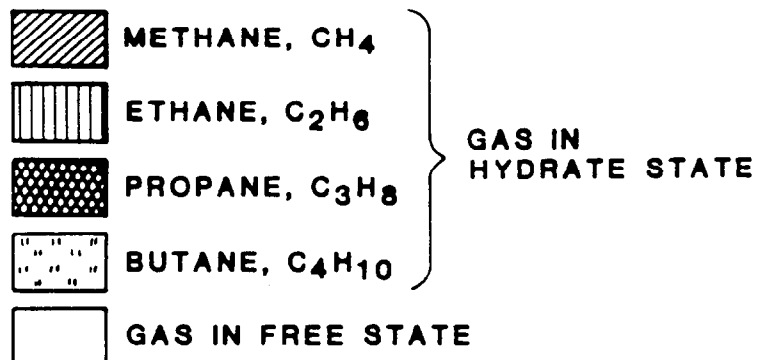
The third series of experiments presented by Makogon (1974) in porous environments were carried out with pure  $\text{CH}_4$ . This allowed for the exclusion of gas differentiation effect during hydrate formation and the examination of factors such as:

- the forces of surface tension on the gas-water-hydrate interface,
- water solubility of gas, and
- coefficients of diffusion.





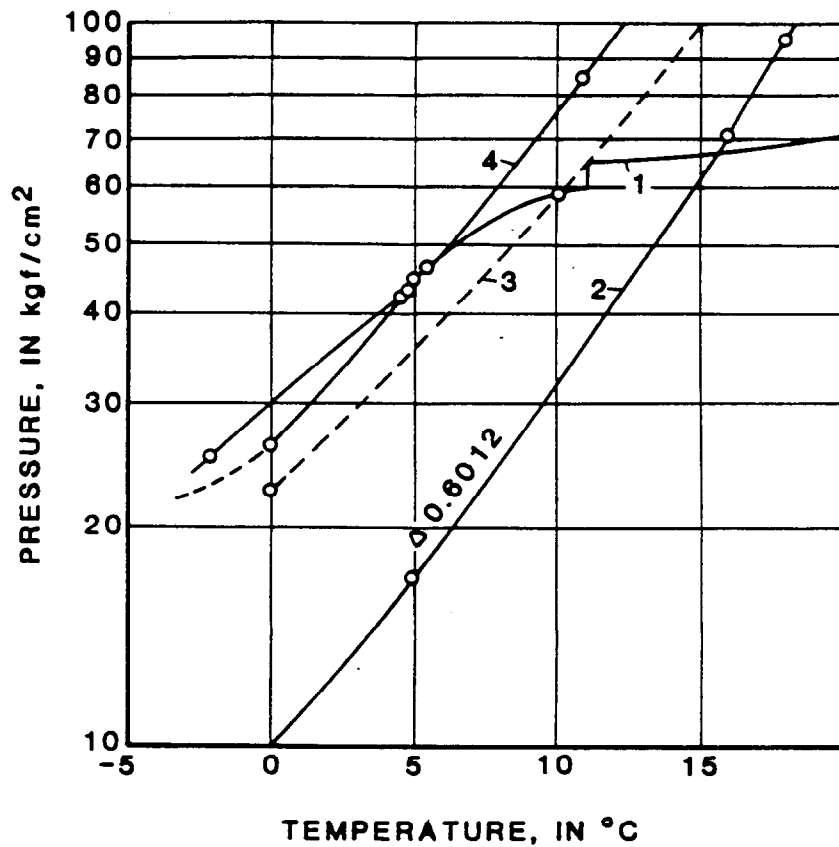
**GAS COMPONENT**



**Figure 14.**

**CHANGE OF GAS COMPOSITION  
DURING HYDRATE FORMATION**

**After Makogon (1974)**



- 1 - Average curve for multi-component gas in a porous medium
- 2 - Curve for multi-component gas in presence of free gas-water interface
- 3 - Curve for methane hydrate formation on free gas-water interface
- 4 - Curve for methane enriched in nitrogen under circumstances of significantly diminished effective capillary radius (porous medium)

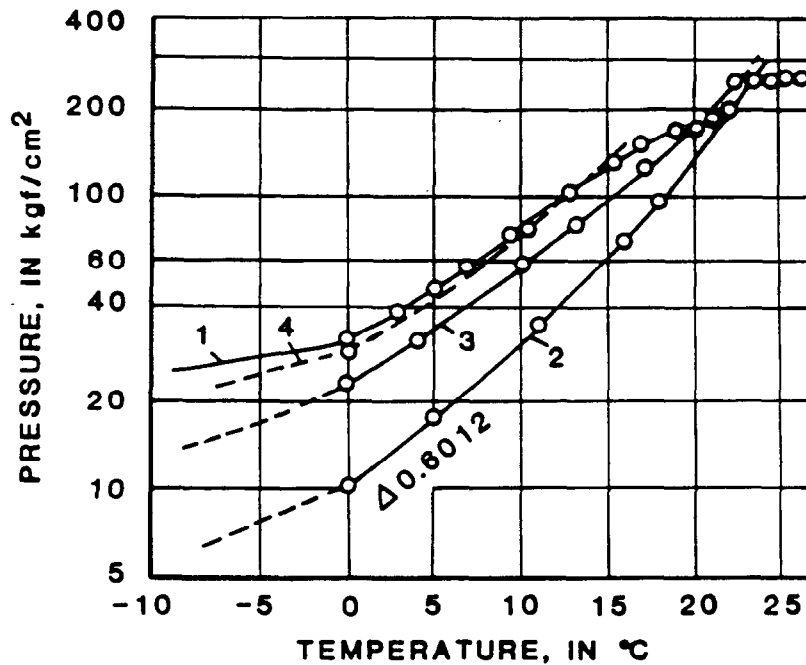
**Figure 15. EQUILIBRIUM CURVES OF NATURAL GAS HYDRATES OF MULTI-COMPONENT GAS IN A POROUS MEDIUM**

**After Makogon (1974)**

TABLE 7.

CHANGES OF VARIOUS PARAMETERS DURING THE FIRST SERIES OF EXPERIMENTS ON GAS HYDRATE FORMATION. After Makogon (1974).

Parameters	Parameter Changes									
	70	64.5	58	44	32	25				
Gas pressure, kgf cm <sup>2</sup>	20	10.5	10	5	1	-2.1				
Temperature, °C	116	117.69	115.84	113.2	110.96	107.73				
Pore volume occupied by gas, cm <sup>3</sup>	9064.6	8808.9	7275.4	5389.1	3793.6	2935.4				
Free gas volume in chamber, cm <sup>3</sup>	--	246.7	1079	3665.3	5260.8	6119.0				
Volume of gas bound in hydrate, cm <sup>3</sup>	--	1.21	8.38	18.62	27.18	31.9				
Water converted into hydrate, g	134	132.79	125.62	115.38	106.82	102.1				
Volume occupied by liquid water, cm <sup>3</sup>		202	200	197	186	182				
Gas : water ratio in hydrates, cm <sup>3</sup> /g										
CH <sub>4</sub>	92.14	92.99	93.73	98.05	97.3	96.6				
C <sub>2</sub> H <sub>6</sub>	5.05	5.07	4.78	--	--	--				
C <sub>3</sub> H <sub>8</sub>	1.27	0.61	--	--	--	--				
C <sub>4</sub> H <sub>10</sub>	0.24	--	--	--	--	--				
N <sub>2</sub>	1.3	1.33	1.49	1.95	2.7	3.4				
CH <sub>4</sub>	--	61.73	63.76	77.12	99.79	99.7				
C <sub>2</sub> H <sub>6</sub>	--	4.22	5.32	22.74	--	--				
C <sub>3</sub> H <sub>8</sub>	--	24.97	30.8	--	--	--				
C <sub>4</sub> H <sub>10</sub>	--	8.94	--	--	--	--				
N <sub>2</sub>	--	0.11	0.12	0.14	0.21	0.3				



- 1 - Average curve for multi-component gas in a porous medium
- 2 - Curve for multi-component gas in presence of free gas-water interface
- 3 - Curve for methane hydrate formation on free gas-water interface
- 4 - Curve for methane enriched in nitrogen under circumstances of significantly diminished effective capillary radius (porous media)

**Figure 16. EQUILIBRIUM CURVES FOR NATURAL GAS HYDRATES OF MULTI-COMPONENT GAS IN A POROUS MEDIUM (OBTAINED DURING SECOND SERIES OF EXPERIMENTS)**

**After Makogon (1974)**

This way, the effect of water vapor pressure lowering on gas hydrate formation could be studied. The results of these experiments are shown on Table 8 and Figure 17. Lowering the temperature along the line AB (Figure 17) is accompanied by nucleation. To initiate hydrate formation (point B on Figure 17) a supercooling of 1.8°C was needed at 118 kgf/cm<sup>2</sup> pressure. The water saturation was 43.3% and the porous medium consisted of sandstone with average grain size of 0.2 mm.

Further temperature lowering along the line CD (Figure 17) shows the influence of solid porous phase on gas hydrate formation compared with the system of a free gas-water contact. At this stage the formation of gas hydrate diminishes the average effective pore radius; and, hence, the influence of the porous medium on the hydrate formation increases (curve section DE on Figure 17).

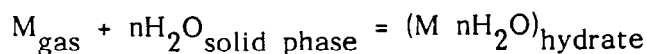
The analyses of the experimental data provided several important conclusions:

1. The influence of porous medium on gas hydrate formation increases with the reduction of average effective capillary radius.
2. This effect is diminished by an increase of pressure.
3. The impact of the porous medium on gas hydrate formation is minimal when water vapor pressure in the pores is equal to or greater than water vapor pressure over the hydrates. If that condition occurs the P-T conditions of hydrate formation are similar to those in free gas-water contact system.

## Thermodynamic Conditions for Gas Hydrate Formation

### Classic Methods of Calculating the Equilibrium Conditions for Gas Hydrates

In the area of gas hydrate thermodynamics, basic elements of consideration are: determination of energy of the hydrate formation, changes of its entropy and enthalpy, work needed in the process of the lattice enlargement. It appears from the Russian literature (e.g. Byk, Makogon, Fomina, 1980) that among classic methods for calculation of the principal thermodynamic parameters, Soviet scientists largely adopted methods developed by von Stackelberg (1954, 1955, 1956) and Truton (1954). Von Stackelberg based his calculation of the entropy of gas hydrate formation on the assumption that the entropy of the reaction



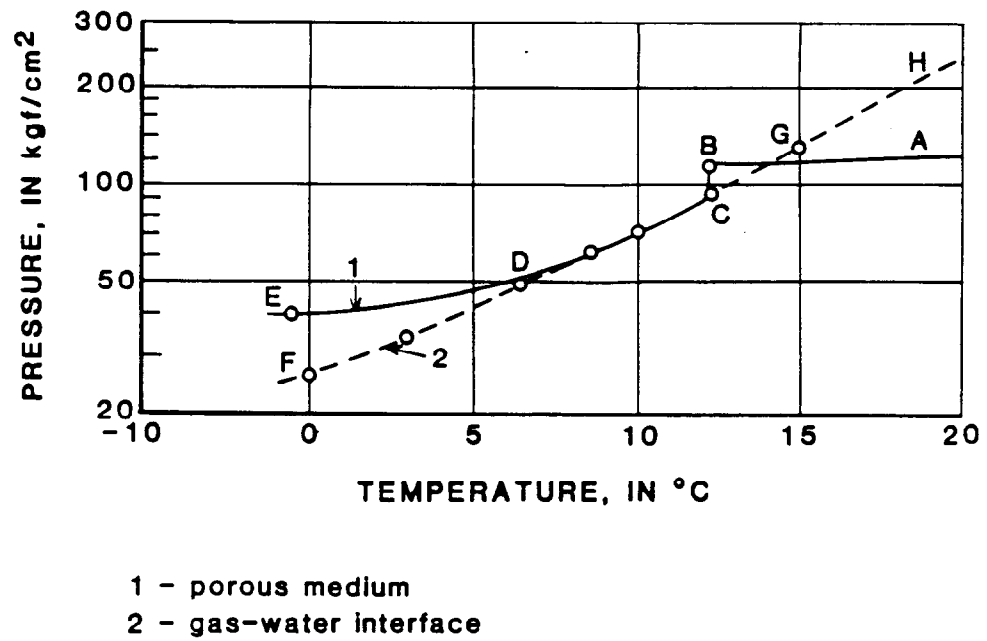
is equal to the entropy change ( $\Delta S$ ) of freezing of 1 mole of gas, where

$$\Delta S = \Delta S_1 + \Delta S_2$$

TABLE 8.

CHANGES OF VARIOUS PARAMETERS DURING GAS HYDRATE FORMATION FOR PURE METHANE IN A POROUS ENVIRONMENT. After Makogon (1974).

Parameters	Parameter Changes						
Gas pressure, kgf cm <sup>2</sup>	121	118	97	74.5	62	47	44
Temperature, °C	20	12.3	12.3	10	8.5	4.7	1.3
Pore volume occupied by gas, cm <sup>3</sup>	70.28	70.28	67.72	65.04	63.65	62.39	61.93
Free gas volume in chamber, cm <sup>3</sup>	10045	10045	7760.1	5499.4	4348.9	3340	2970
Volume of gas bound in hydrate, cm <sup>3</sup>	--	--	2284.9	4545.6	5696.1	6705	7075
Water converted into hydrate, g	--	--	2284.9	2260.7	1150.5	1003.9	370.0
Volume occupied by liquid water, cm <sup>3</sup>	51.52	51.52	40.04	29.51	22.61	17.34	15.42
Gas:water ratio in hydrate, cm <sup>3</sup> /g	--	--	199	196	195	191	192.7



**Figure 17. EQUILIBRIUM CURVES FOR METHANE HYDRATE FORMATION IN POROUS MEDIUM AND ON GAS-WATER INTERFACE**

**After Makogon (1974)**

In this case the entropy of the condensation of 1 mole of gas ( $\Delta S_1$ ) according to Truton (1954) equals -87.8 Joule/K, while for freezing of 1 mole liquified gas it is equal -4 Joule/K ( $\Delta S_2$ ). Consequently the value of  $\Delta S$  was obtained as equal to -92.0 Joule/K mole.

The relationship found by Stackelberg between pressure of gas hydrate dissociation ( $P_{diss}$ ) and the boiling temperature ( $T_{boil}$ ) of the gas has the form:

$$\log P_{diss} = 6.8 - 0.32\sqrt{T_{boil}}$$

$P_{diss}$  is defined as the minimum pressure of a gas contained in the hydrate under which the hydrate is stabilized. The above relationship is valid at the temperature 273.16K. For temperatures (T) lower than 273.16K, von Stackelberg proposed the following equation:

$$4.57 \log P_{diss} = 2.0065 - 400\sqrt{T_{boil}} - 1437n + 22T + 1437 \frac{T}{273}$$

n = amount of water per 1 mole of gas, mole

He calculated  $P_{diss}$  for some well known hydrates at a temperature of 273.16K and compared these results with the experimental data (Table 9). The importance of  $P_{diss}$  value stems from the fact that one of the major conditions of gas hydrate stability is that

$$P_{diss} < P_M$$

where  $P_M$  represents pressure of saturated vapor of the hydrate gas.

TABLE 9.

DISSOCIATION PRESSURES ( $P_{diss}$ ) FOR GAS HYDRATES OF SOME HYDROCARBON GASES. After M. von Stackelberg (1954).

Gas	Boiling temperature K	Dissociation pressure kPa	
		Experimental	calculated
CH <sub>4</sub>	112	2630	2630
C <sub>2</sub> H <sub>6</sub>	171	560	430
C <sub>3</sub> H <sub>8</sub>	180	530	320
C <sub>4</sub> H <sub>10</sub>	228	172	91.2

Using the combined Clapeyron and Truton's equation

$$\log P_M = 6.6 - 0.0169 T_{boil}$$

Von Stackelberg was able to obtain the limit of thermal conditions for possible gas hydrate formation, i.e. where  $P_M = P_{diss}$ . In this way he found



that gases with boiling temperature higher than 331.1 K cannot form hydrates. Through calorimetric and extensometric measurements von Stackelberg showed that for the reaction  $M_{\text{gas}} + n\text{H}_2\text{O} = (M \cdot n\text{H}_2\text{O})$ , the enthalpy for  $n = 6$  varies from -58.6 to 71.1 K Joule/mole, while for  $n = 17$  it ranges from -121.3 to 133.9 K Joule/mole.

Another scientist whose work in the area of gas hydrates entropy calculations gained acceptance among Russian specialists (Byk, Makogon, Fomina, 1980) is Romanian physicist L. G. Yonescu. In collaboration with Russian scientists (Byk, Makogon, Jonescu, 1978) he calculated the entropy of hydrate formation for several gases, among which were  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_2\text{H}_4$ .

It has been known that work of crystalline hydrate cell enlargement due to the entry of gas molecules of bigger size may serve as a criterion of hydrate stability. Work of enlargement of the crystalline cell increases chemical potential of the gas molecule. This fact, in turn, is closely related to the increase of hydrate dissociation pressure ( $P_{\text{diss}}$ ) and consequently to the lowering of the critical temperature of its stability (von Stackelberg, Jahns, 1954). The methodologies to calculate the work of enlargement of the hydrate cell, developed by von Stackelberg (1954), Jahns (1954), McInture and Petersen (1967) have been extensively used in Russian investigations in the area of the gas hydrate thermodynamics (Byk et al., 1980).

#### Statistical Methods of Calculating Equilibrium Conditions for Gas Hydrates

Makogon (1974) acclaims the methods based on the statistical theory of non-stoichiometric clathrates to be the most accepted in calculating equilibrium conditions of gas hydrate formation. The applications of the statistical thermodynamics principles in the gas hydrate field were first shown by van der Waals and Platteeuw (1958). They used a clathrate model of fluids developed by Lenard-Jones (1937) in the statistical description of gas hydrate crystallization. During 1958 - 1962 statistical mechanics applied was in hydrate research conducted by Barrer (1957, 1962) Stuart (1957) and Ruzicka (1962).

The common difficulty in application of these statistical methods is calculation of the Langmuir's constants for individual gases. Calculation of these constants amounts to determining of other constants "A" which represent several molecular parameters. Russian authors like Byk, Fomina, Makogon used in their research three methods of approximation in determination of the constants "A":

a. London's method

$$A = \frac{3}{2} \alpha_1 \alpha_2 \frac{I_1 I_2}{I_1 + I_2}$$

b. Kirkwood-Müller's method

$$A = -6Nmc^2 \frac{\alpha_1 \alpha_2}{(\alpha_1 / \chi_1) + (\alpha_2 / \chi_2)}$$

c. Sleiter-Kirkwood's method

$$A = \frac{3}{4} \cdot \frac{eh}{m} \cdot \frac{\alpha_1 \alpha_2}{(\alpha_1 / n_1)^{\frac{1}{2}} + (\alpha_2 / n_2)^{\frac{1}{2}}}$$

where:

A = constant

$\alpha_1, \alpha_2$  = polarization capacity

- $I_1, I_2$  = ionization potential  
 $N$  = Avogadro number  
 $m_e$  = electron mass  
 $c$  = speed of light  
 $\chi$  = diamagnetic susceptibility  
 $e$  = electron's charge  
 $h$  = Planck's constant  
 $n_1, n_2$  = number of electrons in outside shells of neighboring atoms

The comparison of the Langmuir's constants obtained from statistical calculations and experiments led the Russian authors to the conclusion that London's method yields the most reliable values of A constant.

Other Russian scientists involved in this field of research were Temkin, Groysman, and Gvanov (Byk et al., 1980). Temkin (1938) first obtained the equation of Langmuir's adsorption. Groysman and Ivanov (1973) calculated with the help of a computer the so-called interval of "free" volume, "g", for the following gases:  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ ,  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{SF}_6$ .

$$g_f = \int_0^{\frac{1}{2}} x^{\frac{1}{2}} \exp \frac{\psi(R) - \psi(0)}{kT} dx$$

where:

- $g_t$  = interval of "free" volume of a gas  
 $x_t$  = molar content of a gas  
 $(R), (0)$  = angles of orientation  
 $k$  = Boltzmann's constant  
 $T$  = temperature, K

Calculation of "g" values enabled Groysman and Ivanov to determine the Langmuir's constants for  $\text{SF}_6$ . Using these values, Groysman and Ivanov calculated the hydrate dissociation pressure at the temperature 270.1 K. The values of dissociation pressure of  $\text{SF}_6$  hydrate obtained mathematically and experimentally turned out to be satisfactorily close to each other ( $P$  calculated = 93.2 kPa while  $P_{\text{diss}}$  experimental = 86.1 kPa). The authors, however, state that the calculations made only for  $\text{SF}_6$  gas hydrate may not serve as reliable values of Langmuir's constants for hydrates of other gases.

The methodology of determination of thermal and pressure equilibrium conditions for gas hydrates based on the statistical theory of non-stoichiometric clathrates was presented by Makogon (1974). The author pointed out two provisions in the application of the method to gas hydrates:

1. a hydrate formed from a mixture of gases is considered to be a solid solution which follows Raoult's law,
2. adsorption of gas molecules by small and large voids of the hydrate lattice fits Langmuir's three dimensional model, which assumes an ideally localized adsorption of spherical molecules. Langmuir's constants in the equations describing equilibrium of hydrate and gas phases are calculated using methods of statistical mechanics.

The method is based on the equations characterizing the thermodynamic conditions under which hydrates can exist in presence of liquid water or ice. Gas hydrate formation from liquid water at temperatures above  $0^\circ\text{C}$  can be expressed as follows:

$$\ln \frac{P_{ice} H_2O}{P_0 H_2O} = \frac{m}{(1+m)n} \ln \left( 1 - \sum_{A,B,C...} A\Theta_1 \right) + \frac{1}{(1+m)n} \ln \left( 1 - \sum_{A,B,C...} A\Theta_2 \right)$$
 while for hydrate formation from ice at temperatures below 0°C the following formula is valid:

$$\ln \frac{P_L H_2O}{P_0 H_2O} = \frac{m}{(1+m)n} \ln \left( 1 - \sum_{A,B,C...} A\Theta_1 \right) + \frac{1}{(1+m)n} \ln \left( 1 - \sum_{A,B,C...} A\Theta_2 \right)$$
 where:

- $P_L H_2O$  = pressure of saturated water vapor above liquid water,
- $P_{ice} H_2O$  = pressure of saturated water vapor above ice,
- $P_0 H_2O$  = water vapor pressure above the hypothetical unfilled hydrate lattice,
- $A\Theta_1, A\Theta_2$  = extent of filling of small and large voids in the hydrate molecules A,
- A, B, C. = gas molecules entering the hydrate,
- m = the ratio of large and small voids (for structure I, m = 3; for structure II, m = 2,
- n = number of water molecules in the elementary lattice necessary for one molecule of the hydrate forming gas. When all voids are filled with gas in structure I, n = 5.75; in structure II, n = 5.66

The value of "n" can be calculated from the equations shown below.

For hydrate structure I

$$n_I = 46/(2\Theta_1 + 6\Theta_2)$$

For hydrate structure II

$$n_{II} = 136/(8\Theta_1 + 16\Theta_2)$$

where:

$\Theta_1$  = degree of filling of small voids

$\Theta_2$  = degree of filling of large voids

Values of  $P_0 H_2O$  can be derived from the following equations:

for structure I

$$\log P_0 H_2O = 20.224 \log T - \frac{299.84}{T} - 47.35$$

for structure II

$$\log P_{\text{H}_2\text{O}} = 22.094 \log T - \frac{24.098}{T} - 52.715$$

$A\Theta_1$ ,  $A\Theta_2$  are variable and depend on pressure and temperature. Their values can be determined from the equations

$$A\Theta_1 = \frac{C_{A_1} P_A}{1 + C_{A_1} P_A + C_{B_1} P_B + \dots}$$

$$A\Theta_2 = \frac{C_{A_2} P_A}{1 + C_{A_2} P_A + C_{B_2} P_B + \dots}$$

where:

$C_{A_1}$ ,  $C_{B_1}$  = Langmuir's constants for components A and B for small voids,

$C_{A_2}$ ,  $C_{B_2}$  = Langmuir's constants for large voids,

$P_A$ ,  $P_B$  = partial pressure of components A and B in a gas mixture. (in kgf/cm<sup>2</sup>)

Langmuir's constants for an individual component depend on temperature and are determined by the equation as follows:

$$\log C_i = 0.43429 (A - BT)$$

where:

A, B = constant values (Tables 10 and 11),

T = temperature, K

TABLE 10.

LIST OF CONSTANT VALUES (A AND B) FOR CALCULATION OF THE LANGMUIR'S CONSTANTS FOR GAS HYDRATES OF STRUCTURE I. After Makogon (1974).

Component	Small voids		Large voids	
	$A_1$	$B_1$	$A_2$	$B_2$
CH <sub>4</sub>	6.9153	0.03155	6.0966	0.02792
C <sub>2</sub> H <sub>6</sub>	9.4892	0.04058	11.9410	0.04180
C <sub>2</sub> H <sub>4</sub>	18.1735	0.07287	230.2959	0.07287
H <sub>2</sub> S	6.0658	0.01174	4.4568	0.01174
CO <sub>2</sub>	14.9976	0.05884	15.2076	0.05886
N <sub>2</sub>	3.2485	0.02622	3.0116	0.02475

TABLE 11.

LIST OF CONSTANT VALUES (A AND B) FOR CALCULATION OF THE LANGMUIR'S CONSTANTS FOR GAS HYDRATES OF STRUCTURE II. After Makogon (1974).

Component	Small voids		Large voids	
	A <sub>1</sub>	B <sub>1</sub>	A <sub>2</sub>	B <sub>2</sub>
N <sub>2</sub>	3.2485	0.02622	3.0116	0.02475
H <sub>2</sub> S	4.8258	0.00934	2.4030	0.00633
CO <sub>2</sub>	23.035	0.09037	25.2710	0.09781
CH <sub>4</sub>	6.0499	0.02844	6.2957	0.02845
C <sub>2</sub> H <sub>6</sub>	9.4892	0.04058	11.9410	0.04180
C <sub>2</sub> H <sub>4</sub>	18.1735	0.07287	20.2959	0.07287
C <sub>3</sub> H <sub>8</sub>	--	--	18.2760	0.04818
C <sub>3</sub> H <sub>6</sub>	--	--	9.6250	0.01816
iC <sub>4</sub> H <sub>10</sub>	--	--	13.6942	0.02773

After the values of expressions:

$$P_{H_2O} / (P_0 H_2O) \text{ and}$$

$$m / ((1 + m)n) \ln(1 - A\theta_1) + 1 / ((1 + m)n) \ln(1 - A\theta_2) \\ A, B, C, \dots$$

are determined the computation of the hydrate formation temperature (at given pressure) or hydrate formation pressure (at a given temperature) is possible.

The advantage of this method over the one previously presented is that it takes into account the gas composition change both in the free gas and hydrate phases with changing P-T conditions. The impact of gas components heavier than C<sub>4</sub> on gas hydrate formation is not considered in this method.

### Heterogeneous Equilibrium in Gas-Water Systems

The best way of presentation of equilibrium conditions in multi-phase gas-water system are diagrams of heterogeneous equilibrium. These diagrams for gas-water systems are of great value in defining conditions of hydrate formation both on free gas-water contact and in dispersed media. The first such known diagram was submitted by Roozenboom (1918) for hydrates of SO<sub>2</sub> and Cl<sub>2</sub>. It was shown in generalized form by von Stackelberg (1954). Similar diagrams based on experimental data for hydrates of ethane and propane were presented by Roberts, Brownscombe, Hower (1941) and by Reamer, Selleck, Sage (1952).

Russian scientists Fomina and Byk published in 1972 their heterogeneous equilibrium diagram for gas-water system which included the temperature range below 0°C. Probably the best discussion of the heterogeneous equilibrium diagram for methane-ethane-water system in wide spectrum of

temperature and pressure was given by Makogon (1974). Two separate diagrams presented for ethane-water and methane-water systems are shown on Figures 18 and 19.

The diagram for the ethane-water system (Figure 18) represents the relations for gases whose critical temperature is higher than the temperature of hydrate formation. Figure 19 is characteristic of gases with critical temperatures lower than their hydrate formation temperature. Curve OBF<sub>G</sub> shows the relationship between temperature and pressure for the phase change from liquid to ice for pure water. In Figure 19 ABCD represents P-T conditions for gas hydrate formation, and AabC is the gas vapor pressure curve. Line BC defines conditions under which gas hydrates form from gas and water which are both in the vapor state.

A positive derivative ( $\frac{dt}{dP} > 0$  for line AC means that in order to maintain the process of gas hydrate formation at higher temperatures, the pressure has to be increased. The slope of curve Cd depends on changes of the specific volume of the hydrate forming gases it is converted into hydrate. Analytically this slope can be expressed by the formula:

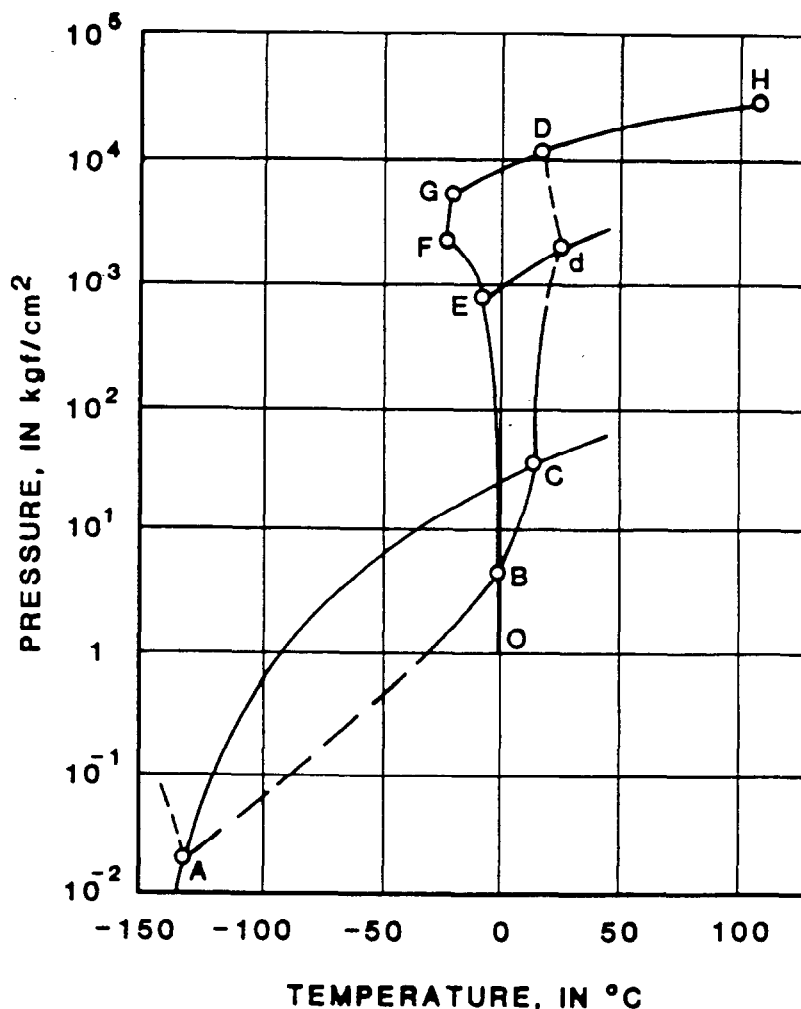
$$\frac{dt}{dP} = \frac{T \Delta V}{Q_r}$$

where:

- T = temperature, K
- $\Delta V$  = change of gas molar volume during its conversion into hydrate
- $Q_r$  = heat of hydrate formation at given temperature, cal
- $\Delta V = V - V_H$
- V = initial molar volume of gas at the equilibrium temperature and pressure
- $V_H$  = molar volume of gas in hydrate

If  $\Delta V > 0$  the curve Cd has a slope to the right (Figure 19), conversely if  $\Delta V < 0$  the slope of Cd is to the left. At relatively low pressure conditions the curve Cd is directed to the right for the hydrates of the following gases: CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, H<sub>2</sub>S and Cl<sub>2</sub>, and it is tilted to the left in case of C<sub>3</sub>H<sub>8</sub> and CH<sub>3</sub>Cl<sub>3</sub>. The curve Cd defines changes of  $\frac{dt}{dP}$  in the neighborhood of point d at which  $\frac{dt}{dP} = 0$ . Therefore, the temperature at point d is critical for hydrates of a given composition. The value of pressure at that point varies for different gases from several atmospheres to several thousands of atmospheres. The temperature of gas hydrate formation drops in higher ranges of pressure values.

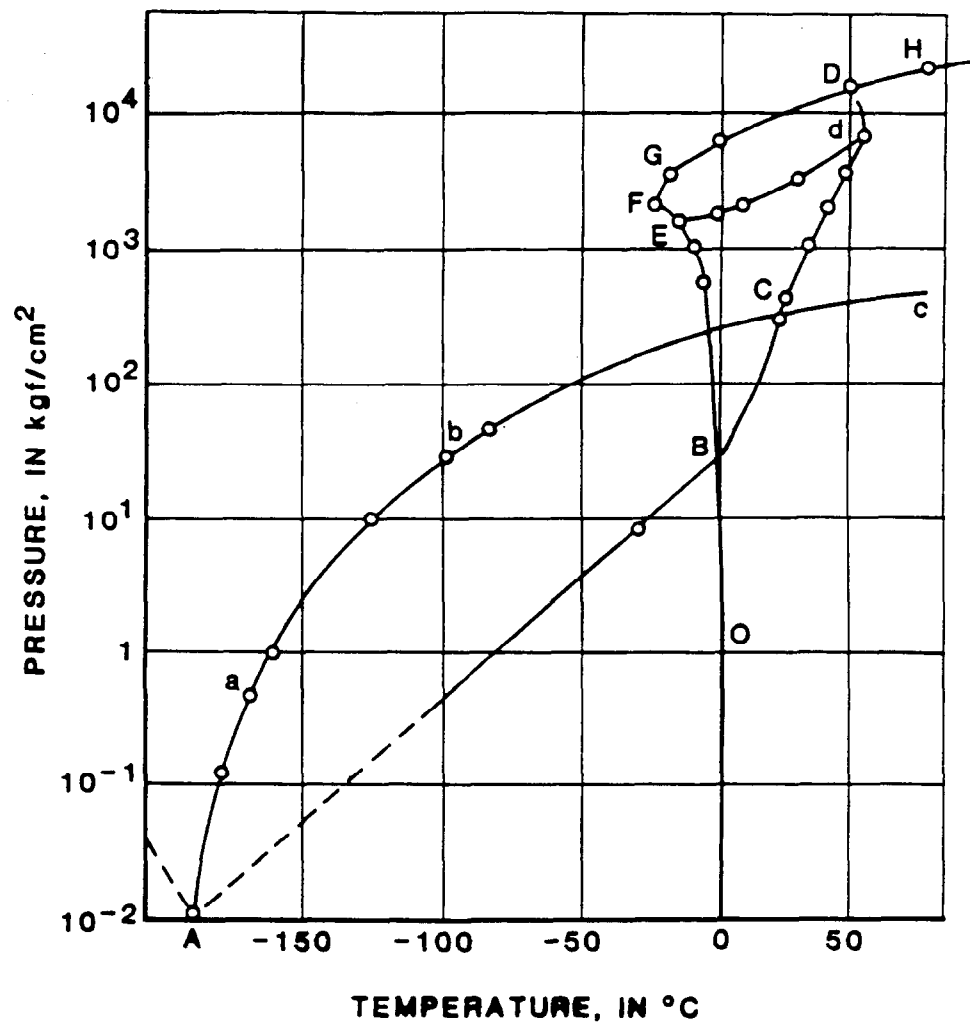
A characteristic feature of the phase diagrams for gas-water systems is the presence of several quadruple points in P-T areas of gas hydrates. There are four quadruple points for gases whose critical temperature is higher than the hydrate formation temperature in the area above 0°C (points A, B, C, D on Figure 18). Point A is located at the intersection of the gas vapor pressure curve and hydrate equilibrium curve at temperatures below 0°C. The second quadruple point, B, is at the intersection of the hydrate



- OFGH - Curve of pure water crystallization
- AC - Vapor pressure curve of the pure hydrate forming gas in function of temperature
- AB - Describes hydrate formation from gas and ice at temperatures lower than 0°C
- BC - Describes hydrate formation from liquid water and gas at temperature above 0°C
- CdD - Describes hydrate formation from water and gas in liquid phase

**Figure 18. PRESSURE-TEMPERATURE DIAGRAM FOR HETEROGENOUS STATE OF THE ETHANE-WATER SYSTEM WHERE  $C_2H_6$  GAS CRITICAL TEMPERATURE IS GREATER THAN THE TEMPERATURE OF ITS HYDRATE FORMATION**

After Makogon (1974)



- OFGH - Curve of pure water crystallization
- AC - Vapor pressure curve of the pure hydrate forming gas in function of temperature
- AB - Describes hydrate formation from gas and ice at temperatures lower than 0°C
- BC - Describes hydrate formation from liquid water and gas at temperature above 0°C
- CdD - Describes hydrate formation from water and gas in liquid phase

**Figure 19. PRESSURE-TEMPERATURE PHASE DIAGRAM FOR HETEROGENOUS STATE OF METHANE-WATER SYSTEM WHERE CH<sub>4</sub> CRITICAL TEMPERATURE IS LOWER THAN THE TEMPERATURE OF ITS HYDRATE FORMATION**

After Makogon (1974)



equilibrium curve with the freezing curve of pure water. At this point gas, water ice, and hydrate are in equilibrium. The point can be readily determined experimentally and analytically. Point C is the third quadruple point. Gas, water, hydrate, and condensed gas are in equilibrium at this point. Many researchers consider the temperature at point C as critical, i.e. a temperature above which the gas hydrates cannot exist. It would be +21.5°C for methane and 14.5°C for ethane. This statement however, is correct only for gases where  $\frac{dt}{dp} < 0$  above point C. The majority of gases display  $\frac{dt}{dp} > 0$  above C. In this respect, the temperature at point C determines only the pressure above which the hydrates can form from the condensed rather than from gaseous phase of gas. The fourth quadruple point (D) is located at the intersection of pure water freezing curve and gas hydrate formation equilibrium curve. At this point ice, water, gas, and hydrate are in equilibrium.

In the case of gases whose critical temperature is lower than the temperature of their hydrate formation only three quadruple points are present (A, B, D - Figure 19). Compared with the diagram on Figure 18, a sharp change of the derivative  $\frac{dt}{dp}$  at the intersection of gas vapor and hydrate formation curves is absent.

During construction of the above diagrams two factors were disregarded:

- a. the influence of the gas solubility in water on its freezing point,
- b. the possibility of new crystal modifications of the hydrates at extremely low temperatures or at high pressures.

### Equilibrium Conditions of Gas Hydrate Formation

For most known gas hydrates, the values of the equilibrium parameters (i.e. pressure and temperature of dissociation) can be drawn from P-T diagrams or equivalent equations. Both the diagrams and the equations are based on the experimental data.

In the Soviet Union experimental gas hydrate equilibrium curves for multicomponent hydrocarbon gases were produced as a result of research conducted by the following scientists: Shakhnazarov (1944); Khodanovich (1946); Strizhev and Khodanovich (1946); Ponomarev (1949); Degtariev, Lutoshkin and Bukhalter (1969); Makogon (1969); Novikova and Vishnevetskii (1969); Siemin (1968); and Byk, Fomina, and Koshelev (1971). Unfortunately most of the publications by the above mentioned authors are not available in the U.S.A. Byk, Makogon, and Fomina (1980) admit however that Russian scientists extensively used the American findings in the area of gas hydrate equilibrium.

For technological purposes mathematical expressions of relationships between temperature and pressure of hydrate formation are very useful. They usually take the form:

$$\log P = at + b$$

where:

P = pressure, kgf/cm<sup>2</sup>  
t = temperature, °C  
a, b = coefficients

Ponomarev (1960) using experimental data obtained the following equations for the equilibrium conditions of hydrates of gases with various relative density:

for temperatures > 273.1 K

$$\log P = 2.0055 + 0.0541(B_1 + T - 273.1)$$

for temperatures < 273.1 K

$$\log P = 2.0055 + 0.0171 (B_1^1 - T + 273.1)$$

where:

P = pressure, kPa  
T<sub>1</sub> = equilibrium temperature of gas hydrate formation, K  
B<sub>1</sub>, B<sub>1</sub><sup>1</sup> = coefficients dependent on relative density of gas (see Table 12)

TABLE 12.

VALUES OF COEFFICIENTS B<sub>1</sub>, B<sub>1</sub><sup>1</sup>, IN PANOMARIEV'S EQUATIONS.  
After Byk et al., 1980.

Relative Density of Gas	Coefficients	
	B <sub>1</sub>	B <sub>1</sub> <sup>1</sup>
0.56	24.25	77.4
0.58	20.00	64.2
0.60	17.67	56.1
0.62	16.45	51.6
0.64	15.47	48.6
0.66	14.76	46.9
0.68	14.34	45.6
0.70	14.00	44.4
0.72	13.72	43.4
0.75	13.32	42.0
0.80	12.74	39.9
0.85	12.18	37.9
0.90	11.66	36.2
0.95	11.17	34.5
1.00	11.77	33.1

Graphical representation of the Ponomarev equations is shown on Figure 20 (after Byk and Fomina, 1971).

Makogon (1962, 1972) and Skhliakho (1972) suggested another equation for calculation of the equilibrium conditions for the hydrates of gases having 0.6 - 1 relative density, at pressures up to 30,000 kPa.

$$\log P = \alpha[(T - 273.1) + k(T - 273.1)^2] + \beta$$

where:

- P = pressure, kPa
- T = temperature, K
- $\alpha$  = equilibrium pressure of gas hydrate formation at the temperature around 273.1 K
- k,  $\beta$  = coefficients from Figure 21.

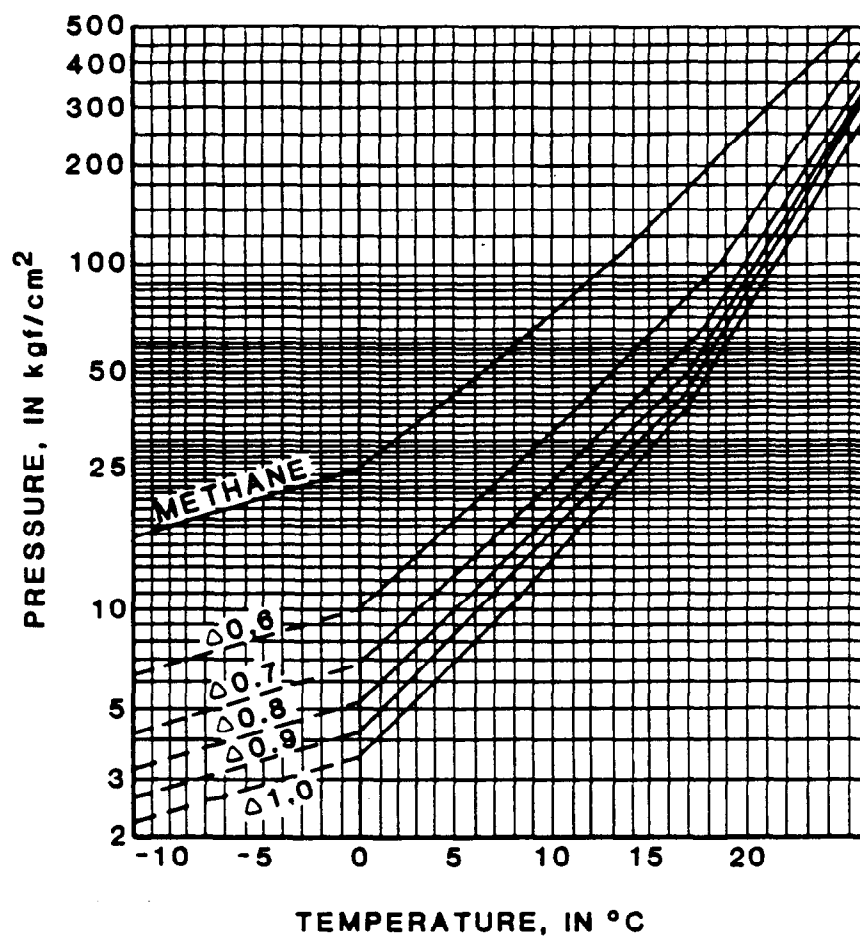
Similar equations for various gases were given by Koshelev, Byk and Fomina (1971), Makogon and Skhliakho (1972; Table 13). The curves on Figures 22 and 23 were constructed for gases with fixed composition, but in reality this composition varies in course of hydrate formation. Therefore, the presented relationships are only approximate.

According to Byk, Makogon and Fomina (1980) the comparison studies of equilibrium P-T parameter values, obtained experimentally and through the thermodynamic calculations showed acceptable closeness for methane and multi-component gas hydrates.

TABLE 13.

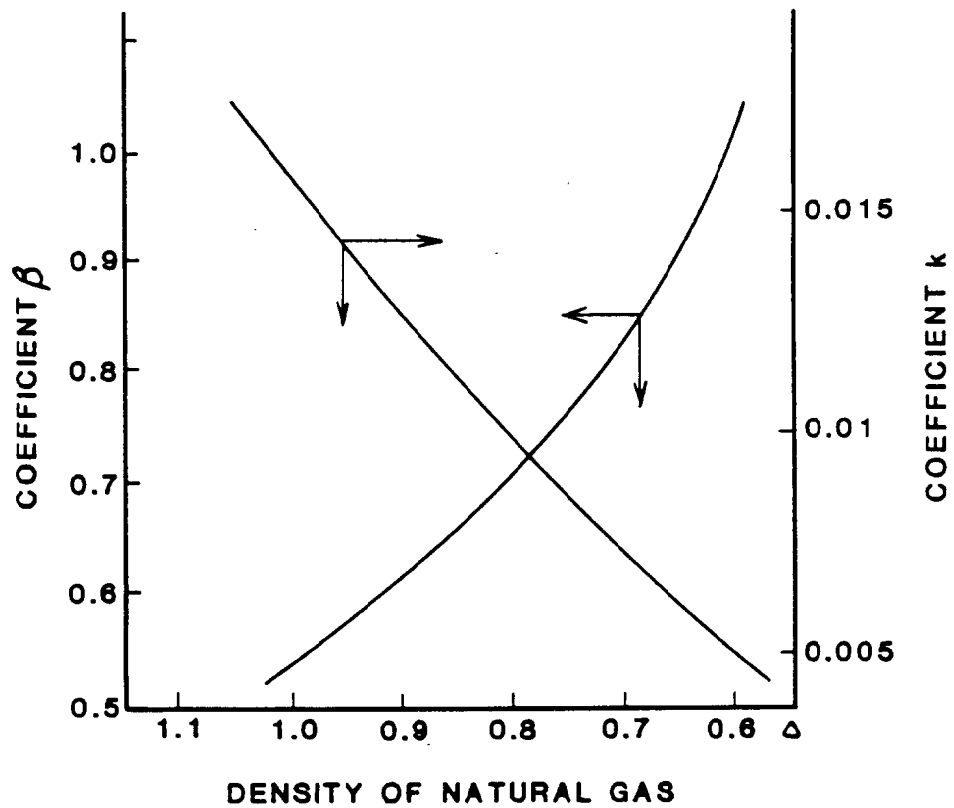
PRESSURE-TEMPERATURE ANALYTICAL RELATIONSHIPS FOR HYDRATE FORMATION OF VARIOUS NATURAL GASES. After Makogon and Skhaliakho (1972); Koshelev, Byk and Fomina (1971).

Gas and its relative density	Temp interval °C	Equation
CH <sub>4</sub>	0 to -11	$\log p = 5.6414 - \frac{1154.61}{T}$
	0 to +23 +24 to +47	$\log p = 1.415 + 0.0417(t + 0.01t^2)$ $\log p = 1.602 + 0.0428t$
C <sub>2</sub> H <sub>6</sub>	0 to -10	$\log p = 6.9296 - \frac{1694.86}{T}$
	0 to +14.5	$\log p = 0.71 + 0.0547t$
C <sub>3</sub> H <sub>8</sub>	0 to -12	$\log p = 5.4242 - \frac{1417.93}{T}$
	0 to +8.5	$\log p = 0.231 + 0.0576t$
CO <sub>2</sub>	0 to -6	$\log p = 13.4238 - \frac{3369.1245}{T}$
	0 to +9.8 +10 to -12	$\log p = 1.08 + 0.056t$
H <sub>2</sub> S	0 to -23	$\log p = 4.8592 - \frac{1334.1919}{T}$
	0 to +29.6 +29.5 to -32	$\log p = 2.844 + 0.0466t$
C <sub>n</sub> H <sub>2n+2</sub> , 0.6-1	0 to +25	$\log p = +0.0497(t + kt^2)$
Shebelin, 0.61	0 to +25	$\log p = 0.085 + 0.0497(t + 0.00505t)^2$
Orenburg	0 to +20	$\log p = 0.891 + 0.0577t$
Urengoi (well #8)	0 to +20	$\log p = 1.4914 + 0.0381(t + 0.0184t)^2$
Urengoi (well #1)	0 to +20	$t = 14.7 \log p - 11.1$
Laq (France)	0 to +23	$\log p = 0.602 + 0.0477t$



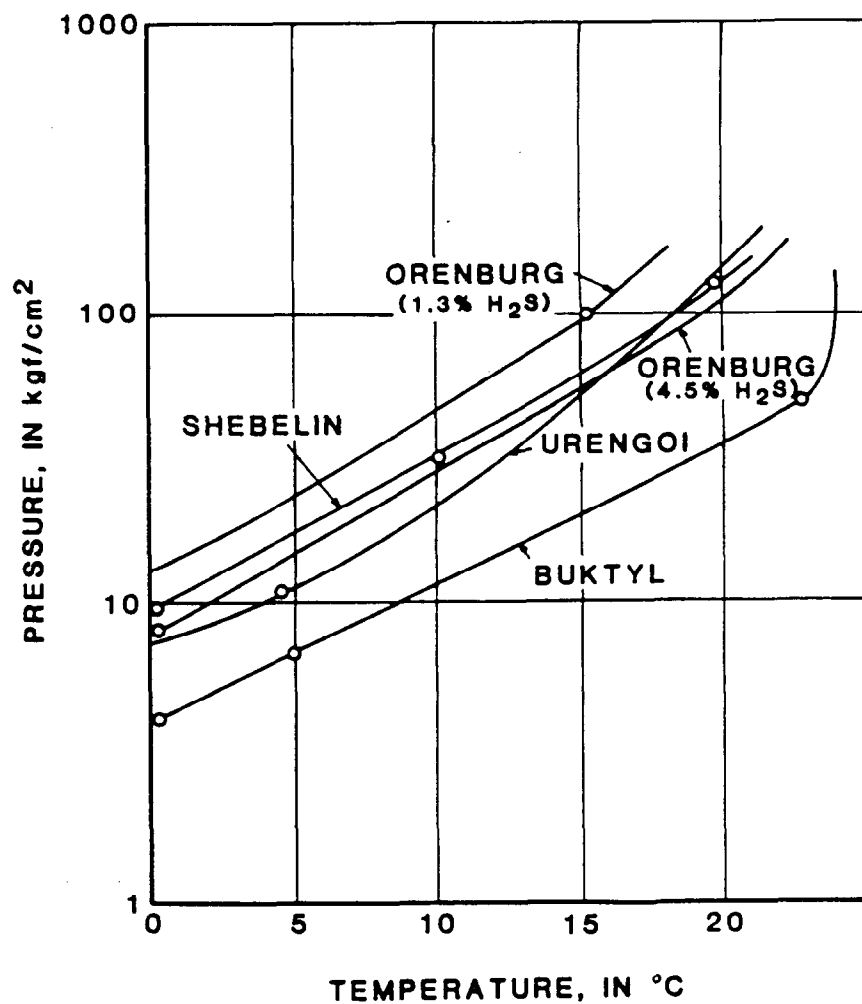
**Figure 20. EQUILIBRIUM CURVES OF HYDRATE FORMATION  
FOR NATURAL GASES OF VARIOUS DENSITIES**

**After Byk and Fomina (1971)**



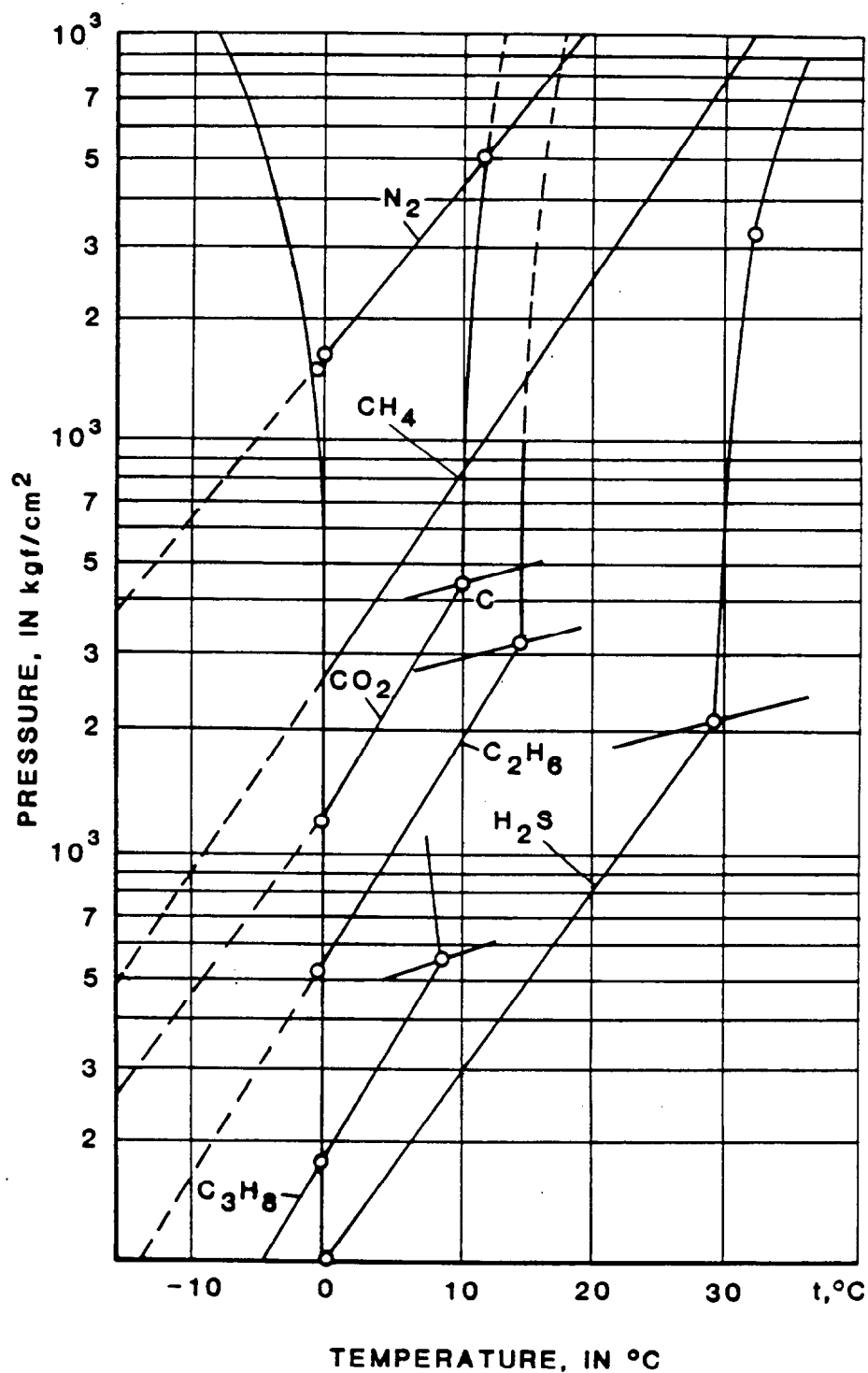
**Figure 21. RELATIONSHIP BETWEEN  $\beta, k$  COEFFICIENTS AND RELATIVE DENSITY OF NATURAL GASES**

**After Makogon (1974)**



**Figure 22. EQUILIBRIUM CURVES FOR HYDRATES OF GASES FROM SOME RUSSIAN GAS FIELDS**

**After Makogon (1974)**



**Figure 23. PRESSURE-TEMPERATURE DIAGRAM FOR HYDRATES OF VARIOUS GASES WITH A FREE GAS-WATER INTERFACE**

After Trofimuk et al. (1978)



## EXPLORATION FOR NATURAL GAS HYDRATE DEPOSITS

Exploration methods are given little consideration in Russian literature and have a very general character. Relevant information is scattered in many papers (Makogon et al., 1971; Makogon, 1974; Trofimuk et al., 1980).

From the reviewed Russian literature in gas hydrates it appears that Messoiaikh and Vilyui fields are at the present time the only known locations in the Soviet Union and in the world with gas production from hydrate deposits. Therefore, they are areas where hydrate exploration methods can be verified. The amount of available Russian information in this area proved to be very limited.

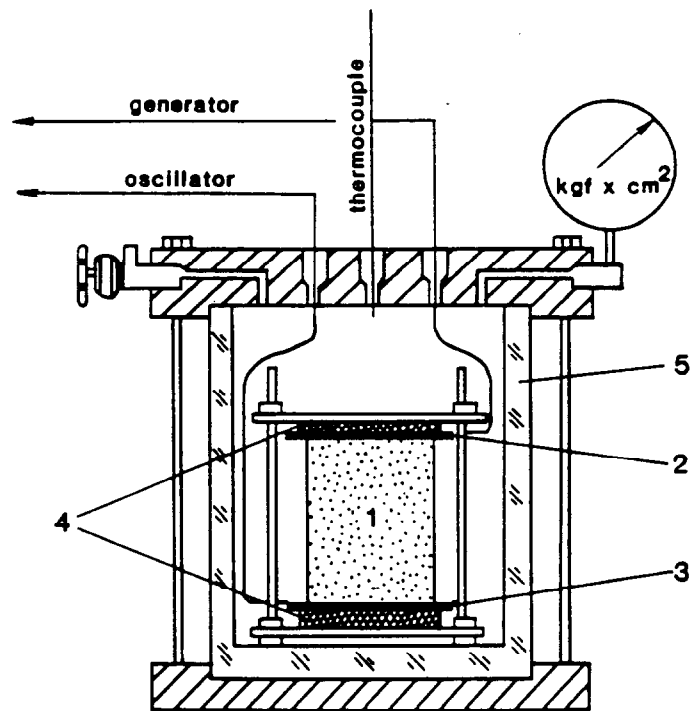
In general three groups of exploration methods for gas hydrate deposits have been recommended in the reviewed Russian literature:

- seismic methods
- geochemical methods
- well logging.

### Seismic Methods

The changes of acoustic wave velocities versus water phase changes were experimentally studied at the Gubkin Petrochemical and Gas Industry Institute in Moscow, using the specially devised equipment shown in Figure 24 (Trofimuk, Cherskii, Tsarev, Borovikov, 1980). The experiments showed a significant increase of acoustic wave velocity as water impregnated samples were transformed into hydrates (Figure 25). It has been found that when the stratal water evolves into hydrates, acoustic velocities increase by about 500 -800 m/s in both cemented and uncemented rocks. In the area of the influence of such factors as grain size, porosity and density of marine sediments on the travel time of elastic waves, Russian scientists (Trofimuk et al, 1980) refer to the publication by Smith (1977; Figure 26). Smith showed that change of the acoustic velocity due to those factors is considerably smaller than increase of the velocity in the hydrate containing formation. Therefore it has been generally accepted that acoustic methods can be effectively used in exploration for gas hydrates.

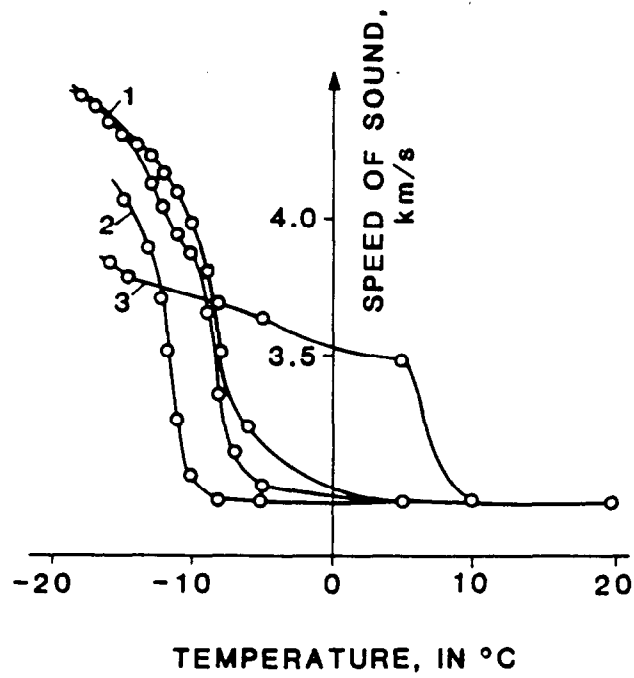
According to Trofimuk et al. (1980), in marine sediments the top of the hydrate zone usually has much less transitional character than the base of the zone. Therefore, the strongest seismic response will be obtained from the top surface of the gas hydrate zone. Those authors recommended high resolution acoustic methods and seismic profiling with working frequency 10 - 12 kHz with penetration capabilities of 5 - 20 m for identifying the hydrate horizons. The transition zone from non-hydrate to hydrate containing sediments at the base of the hydrate zone may be 100 m thick (Trofimuk et al., 1980). In



- 1 - rock sample
- 2 - acoustic emitter
- 3 - acoustic receiver
- 4 - absorbers
- 5 - chamber wall

**Figure 24. SCHEMATIC DIAGRAM OF APPARATUS FOR STUDYING THE ACOUSTIC PROPERTIES OF ROCKS**

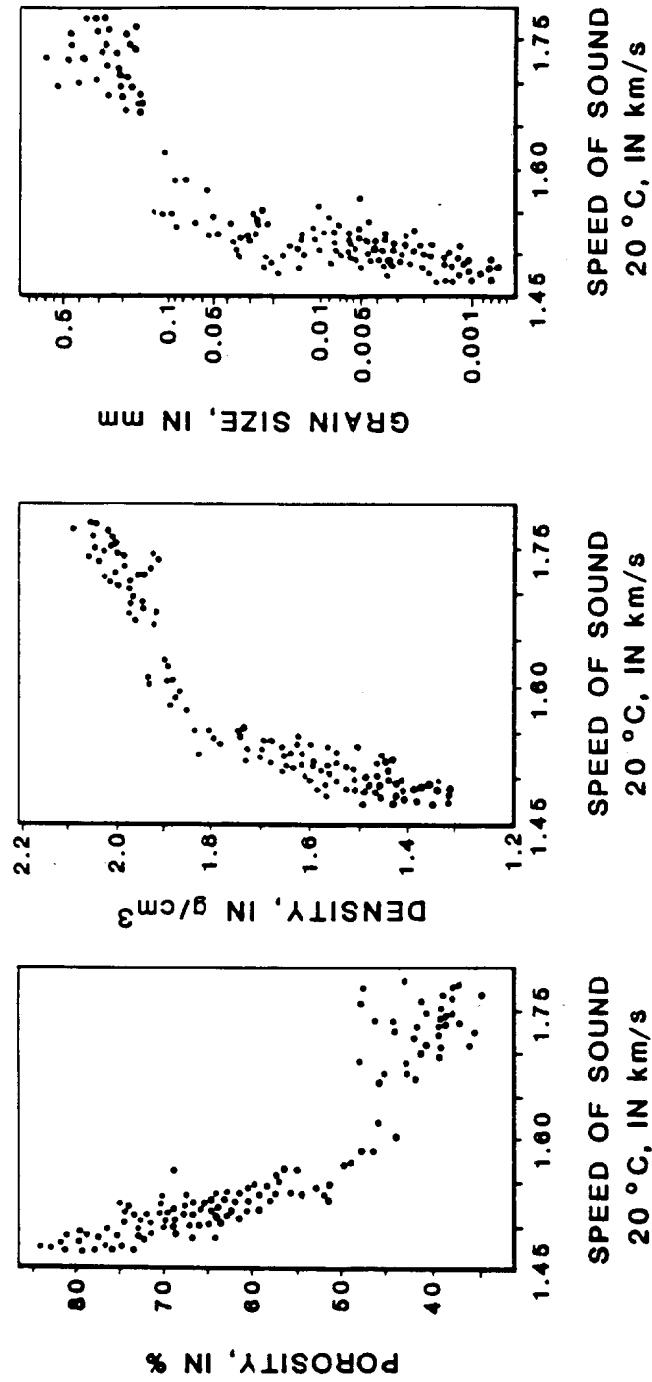
**After Trofimuk et al. (1980)**



- 1 - water
- 2 - ice
- 3 - hydrate-water

**Figure 25. RELATIONSHIP BETWEEN VELOCITY OF ELASTIC WAVES AND PHASE OF PORE FLUID**

**After Trofimuk et al. (1980)**



**Figure 26. ELASTIC WAVE VELOCITY IN SEDIMENTS IN FUNCTION OF THEIR POROSITY, DENSITY, AND GRAIN SIZE**

After Smith (1977)

such cases the hydrate zone may not appear on seismic profiles. The Russian authors also indicate that only in extreme situations, either when there are rocks saturated with free gas immediately below the gas hydrate zone or when mineral associations display sharp changes, can the seismic surfaces be detected. In order to fulfill the task of locating bases of gas hydrate zones at depths of 300 - 400 meters below sea bottom they recommended to use seismic profilers with working frequencies of 100 - 300 Hz.

With all presented recommendations by Russian scientists there is no real evidence of applied seismic methods in the hydrate exploration in their publications. No example of seismic sections or profiles with the indications of gas hydrate presence has been shown in all reviewed Russian materials.

### **Geochemical Methods**

As discussed in the chapter of this report, "Hydrocarbon generation and gas solubility in water", the methane generation zone and hydrate zone lie several centimeters to several meters below sea bottom (Cherskii and Trofimuk, 1977). Because of these rather shallow gas occurrences, direct geochemical methods can be applied. Among these methods Russian authors point at collection of marine sediment samples and measurement of their gas content (Trofimuk et al., 1980). According to these authors, using ground coring tubes, the cores can be collected from subbottom depths up to 5 - 8 meters and in some instances to 12 meters, penetrating the methane generation zone and reaching tops of the hydrates.

Trofimuk, Cherskii, and Tsarev (1980) attempted to find the maximum amount of gas which can be brought up to the surface from its original strata in a non-hermetic core barrel. Gas content higher than the maximum value may indicate the presence of gas hydrates. In their calculations authors assumed porosity of sediment 30 - 50%, where methane content should be 270 - 700 cm<sup>3</sup> per liter of sediment. Such gas content corresponds to 900 - 1,400 cm<sup>3</sup> of CH<sub>4</sub> in 1 liter of pore water. The calculations showed that the maximum volume of gas recovered from a non-hermetic core barrel based on these assumptions can be 250 cm<sup>3</sup> per 1 liter of sediment. Only in the case of strongly compacted sediments can the above figure be higher. The results of the gas volume calculations proved to be in full agreement with field data from Lake Baikal. Trofimuk and his co-workers (1980) pointed out that using a non-hermetic core barrel can provide only qualitative data as to its original content in the formation. No indication of using a pressure core barrel (PCB) in the Soviet Union was found in the reviewed Russian literature.

### **Well Logging**

Although there are a number of Russian publications directly related to the permafrost in north and northwestern Siberia, well-log documentation is sparsely represented in the Soviet literature. In some cases the authors

discuss characteristic features of well logs, where the boundaries of the permafrost can be clearly distinguished. Dyakonov (1958) showed that the best results in delineating the permafrost thickness can be obtained from open-hole temperature logging. Dostovalov (1955), Akimov (1959) and Ostriy and Cherkashin (1960) pointed out that electric resistivity and caliper logging can also yield good results. Figure 27 shows several examples of well logs with noticeable boundaries of permafrost from Eloguyskoi gas field in northwestern Siberia.

Short discussions of well log features in gas hydrate zones have been presented by Sheshukov (1972), Sapir (1973), Makogon (1974) and Trofimuk, Cherskii, Tsarev and Nikitin (1982). Characteristic logs from the sandstone of Cenomanian age in the Messoiakh field, containing gas hydrates are shown after Sheshukov (1973 - simplified logs) and Sapir (1973 -logs from well No. 136 on Figures 28 and 29).

On **resistivity electric logs**, strata with gas hydrates often display high and low values as well (Trofimuk et al., 1982). This is mainly due to two factors:

- a. relative content of solid, fluid and gaseous phases in the strata, and
- b. formation water mineralization.

In the opinion of Trofimuk, Cherskii, Tsarev, and Nikitin (1982), the fact of unreliability of the resistivity log necessitates using it in conjunction with other logging measurements.

**The spontaneous potential (SP)** measurements in the gas hydrate zone show smaller amplitudes compared with sections saturated with water or gas. They do not display, however, the features of compacted impermeable rocks. For more detailed determination of reservoir quality features, the Russian authors recommend the treatment of the hydrates with methanol several times and running an SP log after each treatment.

The **microresistivity logs** in the hydrate zone display features of solid compacted formation.

**Gamma-ray logs** of strata saturated with the gas hydrates show low values, i.e. similarity to gas saturated formations. In the Soviet Union, gamma-ray logging is consistently applied in all exploratory wells.

On **neutron-gamma logs** the gas hydrate zone does not differ in character from the water saturated zones. After treatment with methanol, the hydrate saturated horizons display gas content while aquiferous strata do not show any change.

**Caliper log** usually shows significant deflection due to enlargement of the hole diameter in the intervals of gas hydrates.



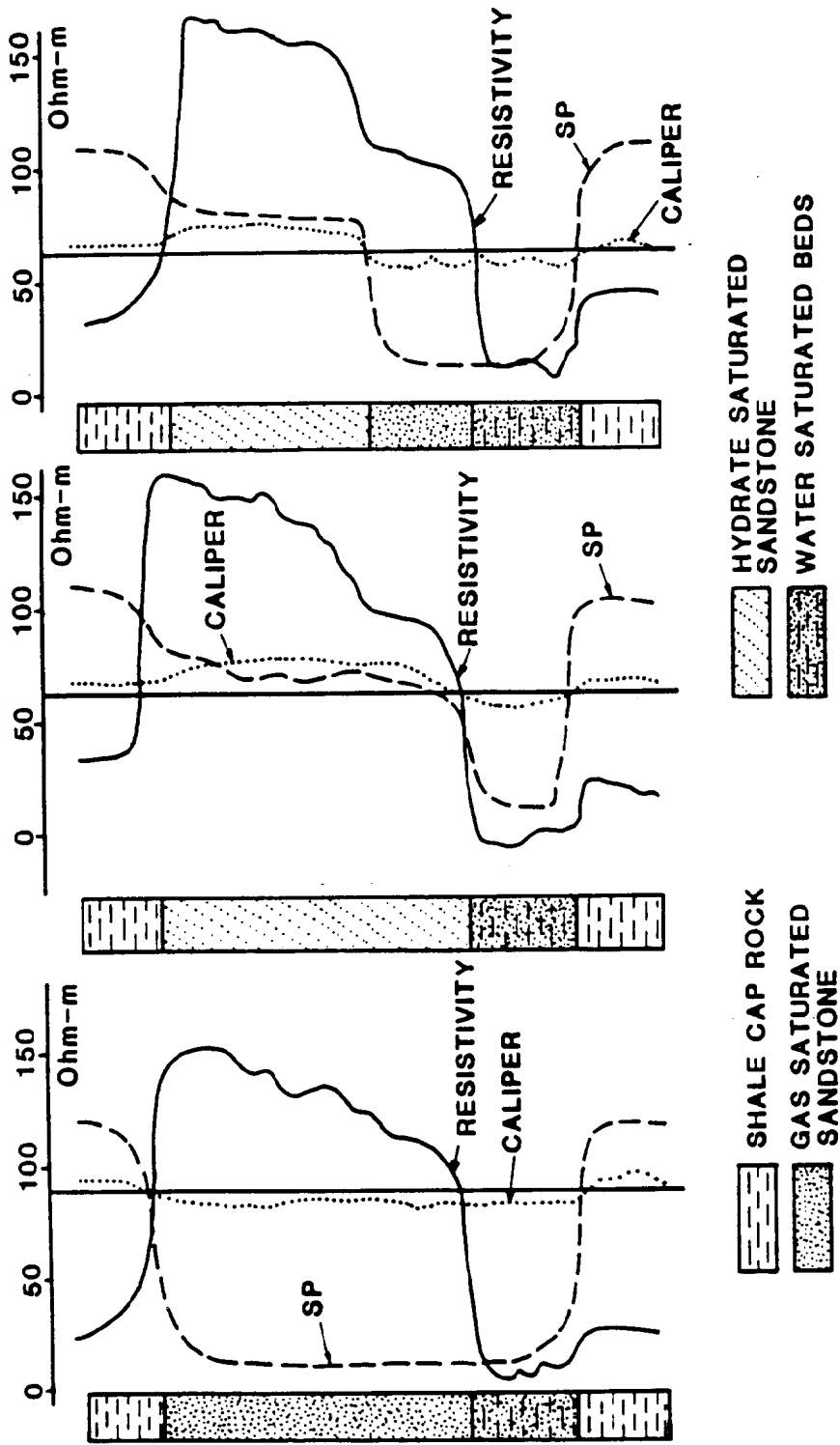


Figure 28. CHARACTERISTIC GEOPHYSICAL FEATURES OF STRATA CONTAINING GAS HYDRATES

After Sheshukov et al. (1973)



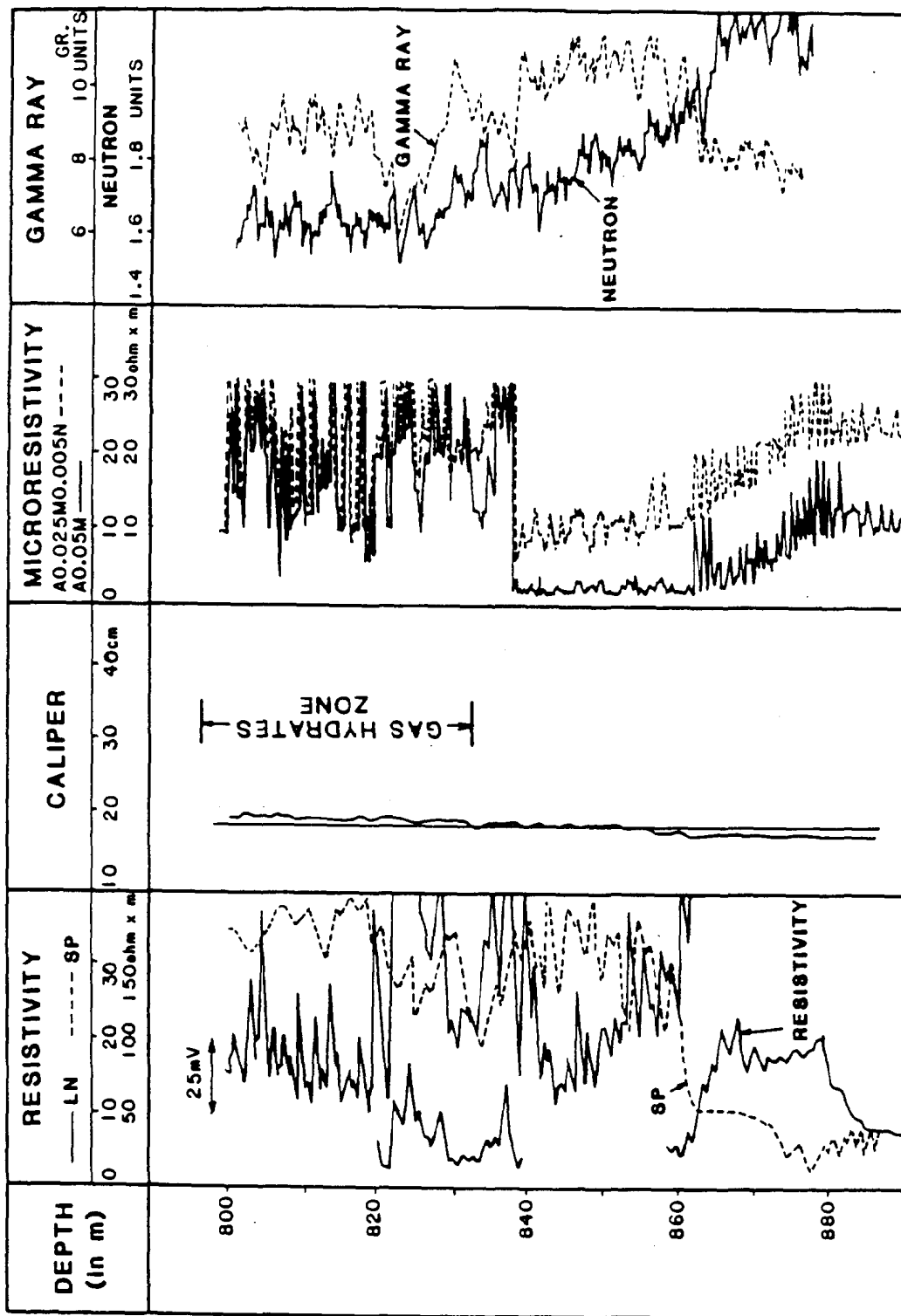


Figure 29. WELL LOGS FROM WELL NO. 136 OF THE MESSOIAKH FIELD

After Sapir (1973)

## OCCURRENCES OF NATURAL GAS HYDRATES

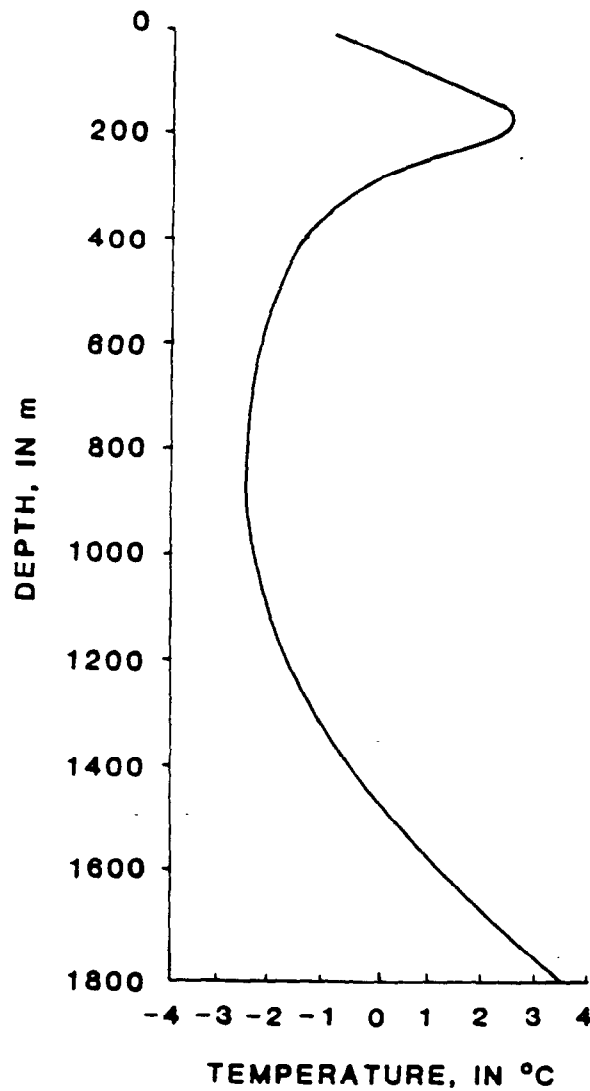
The presence of natural gas hydrates coincides with the areas where thermodynamic conditions are within the equilibrium limits for their formation in a porous medium. Significant differences exist between continental and marine gas hydrates regarding their formation and the degree of their understanding. In Russian literature several authors have discussed the subject of gas hydrate occurrence. A majority of the published works from this area are related to the continental gas hydrates (e.g. Makogon, 1965, 1974, 1984; Sapir et al., 1973; Sheshukov et al., 1972; Sheshukov, 1973; Makogon et al., 1971; Sumetz, 1974; Byk et al., 1980; Trofimuk et al., 1980; Trofimuk et al., 1981; Barkan and Voronov, 1982). The subject of marine gas hydrates has substantially less representation in Russian literature (e.g. Makogon et al., 1973; Makogon, 1974; Trofimuk et al., 1978).

### Continental Gas Hydrates

Natural gas hydrate deposits in continental areas are usually confined to regions of permafrost as defined by their geothermal profiles. Permafrost covers 23% of continents, occupying 73% of the territory of Alaska, 63% of Canada and 47% ( $10.6 \times 10^6 \text{ km}^2$ ) of the USSR (Makogon, 1974). The depth of permafrost occurrence as stated by Makogon (1974) may reach 500 - 700 m and in some instances more than 1,000 meters. This fact was documented in the Markhpisk well in northwestern Yakutia where  $0^\circ\text{C}$  was measured at a depth of 1,400 m (Figure 30).

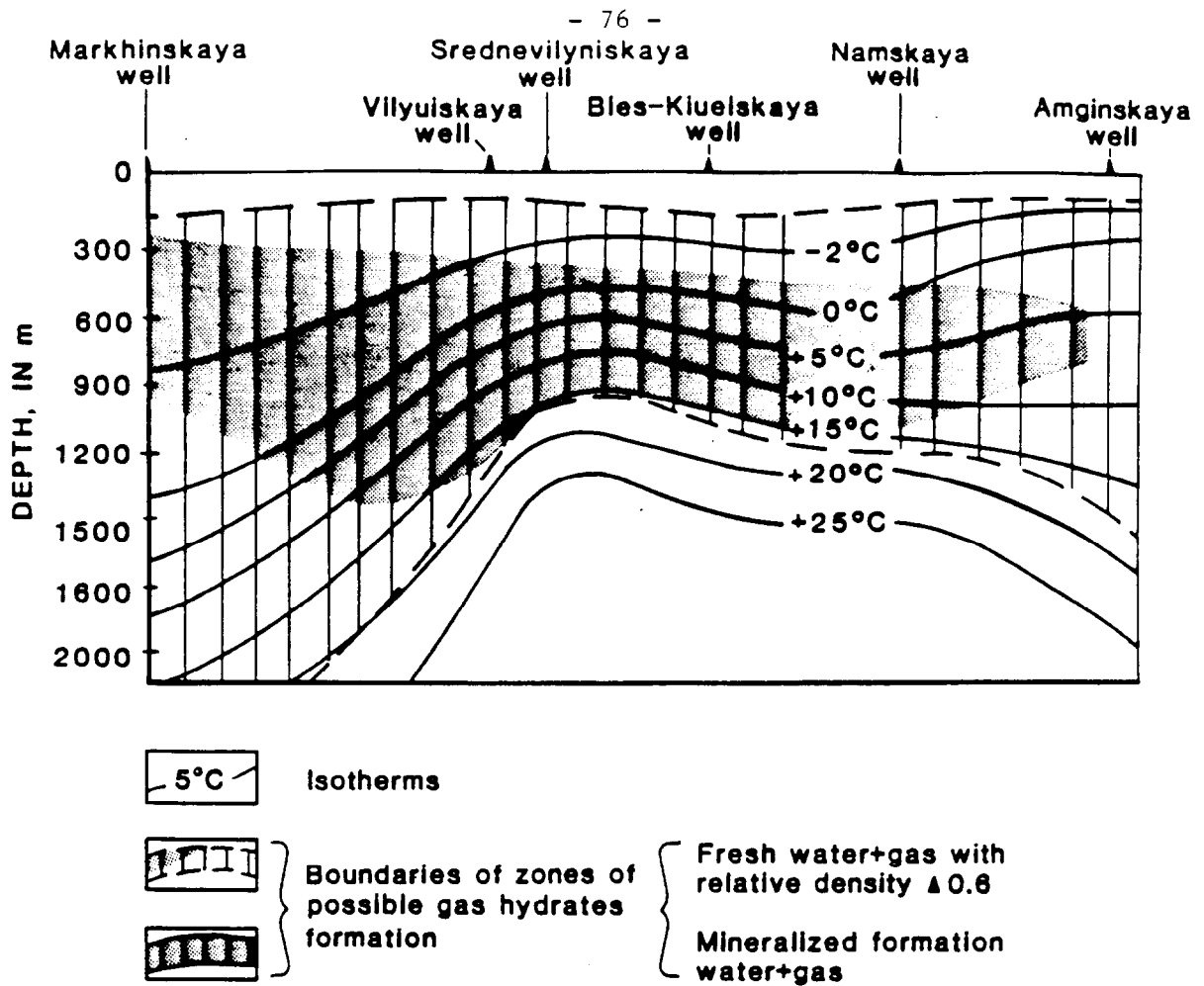
The presence of permafrost is determined by actual and paleo-heat flux which is controlled by such factors as depth to crystalline basement, structural features of the area, type of rocks and their thermal properties, present and paleo-climatic conditions. Russian investigations showed that the lower limit of the gas hydrate zone, although generally following the geothermal lines, does not conform with them totally (Figure 31) because other factors besides temperature play a role in the process of gas hydrate formation (Makogon, 1974; Trofimuk and Tolkatchev, 1981). Consequently the area of hydrate occurrence may exceed the limits of permafrost development. For instance, some of the natural gas deposits in the Orenburg Province (e.g. Orenburg and Sovkhoz fields) are probably in the hydrate state (Makogon, 1974).

Based on various Russian studies, the first map with zones of favorable conditions for gas hydrate formation in the USSR was prepared by Makogon



**Figure 30. THERMOGRAM FROM THE MARKHPISK WELL NO. 1  
IN NORTHWESTERN YAKUTIA**

**After Makogon (1974)**



**Figure 31. CROSS-SECTION OF YAKUTIA WITH ZONE OF THE NATURAL GAS HYDRATES OCCURRENCE**

**After Trofimuk and Tolkatchev (1981)**

(1974; Figure 32). An important assumption was made that the conditions for hydrate formation in porous medium are similar to those on free gas-water contact. Two other Russian scientists, Barkan and Voronov (1982), released their map of gas hydrate distribution in the USSR (Figure 33). Their map was constructed on the base of statistical calculations of equilibrium conditions for gas hydrates and on analyses of geochemical and hydrogeological data from major oil and gas provinces. The southern boundary of the possible hydrate zone was delineated after defining it as the line of 500 m minimum depth from the surface to the bottom of the hydrate zone. The map shows that the possible zones of gas hydrate occurrence are widely spread in the Leno-Tunguskoi and Khatangsko-Vilyuiskoi oil and gas provinces of Eastern Siberia. A characteristic feature common for all these regions is the presence of permafrost. In Yakutia and Putorana Plateau the permafrost zone attained its maximum thickness. The thickness of the zone diminishes from north to south. In almost the entire area the geothermal gradient does not exceed 1.5°C per 100 m. The exception is the northwestern part where it reaches 2.5 - 3°C and more per 100 m.

In the sedimentary mantle of the area, the formation water is highly saline and contains dissolved gases, mainly methane.

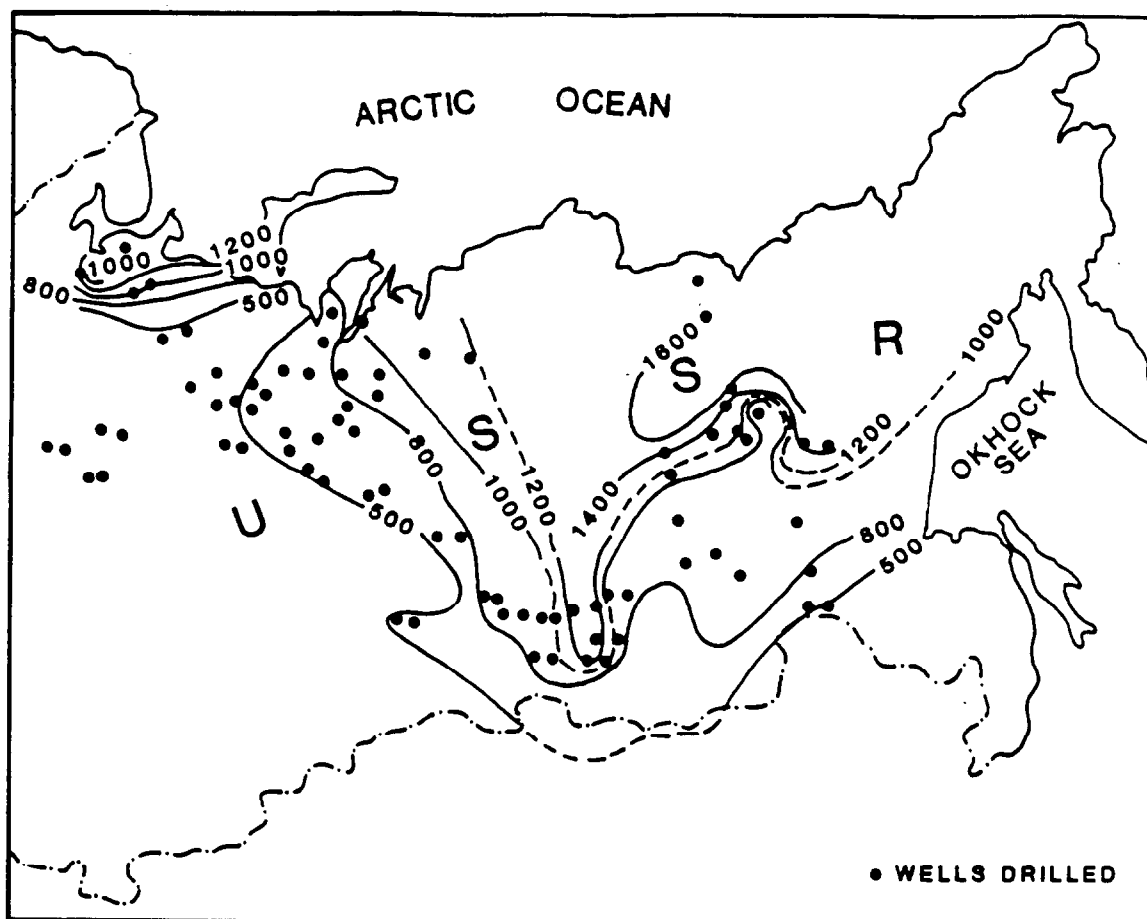
Barkan and Voronov (1982) found out that the gas hydrate zone in the territory of the USSR is developed in four oil and gas provinces (Lena-Tunguskaya, Khatangsko-Vilyuiskaya, West Siberia, Timano-Pechorskaya) and in four separate districts (Momo-Zirianskii, Novosibirskii, Peshinskoye-Pustoret'skii, and Anadirskii). Its total distribution area reaches  $3.4 \times 10^6$  km<sup>2</sup>. According to these authors it is reasonable to expect an increase of gas reserves in the areas shown on the map, due to higher gas concentration and the lower degree of gas diffusion.

Some data on the thickness of the permafrost and the depths of expected hydrates in eastern Siberia and Alaska had been shown by Makogon (1974; Tables 14 and 15).

Virtually the only localities described in the Russian literature, with respect to naturally occurring gas hydrate deposits are the Messoiakhs and Vilyui fields.

### **Messoiakhs Natural Gas Hydrate Deposits**

The Messoiakhs field was discovered in 1967. It is located in the northeastern part of West Siberian oil and gas province (Barkan and Noronov, 1982) about 250 km west of the city of Noril'sk (Figure 34). Geologically the field is located in the Yenisei-Khatang trough (Sapir et al., 1973). Probably the fullest available descriptions of the gas producing horizons in the area have been presented by Sheshukov et al. (1972) and Sapir et al. (1973). In accordance with those descriptions the gas producing structure of the Messoiakhs field consists of a brachyanticline which is elongated in a west-east direction. Hydrocarbons have been found in the Dolgan Sandstone of Albian-Cenomanian age, at depth of 800 - 890 m. Porosity of this formation varies from 16% to 38%, averaging 25% while permeability is approximately 125 mD. Water saturation ( $S_w$ ) in Dolgan Sandstone reaches 29 - 50% with an average value of 40% and its salinity exceeds 1.5% (Sheshukov et al., 1972). Analyses of gases averaged 98.6% methane, 0.1% C<sub>2</sub>-nC<sub>4</sub>, 0.5 CO<sub>2</sub> and 0.7 N<sub>2</sub> (Makogon, 1984). Formation pressure at the top of the pay zone is



**Figure 32. DISTRIBUTION AND LOWER DEPTH LIMITS OF ZONES OF POTENTIAL GAS HYDRATE FORMATION IN CONTINENTAL AREAS OF THE USSR**

**After Makogon (1974)**

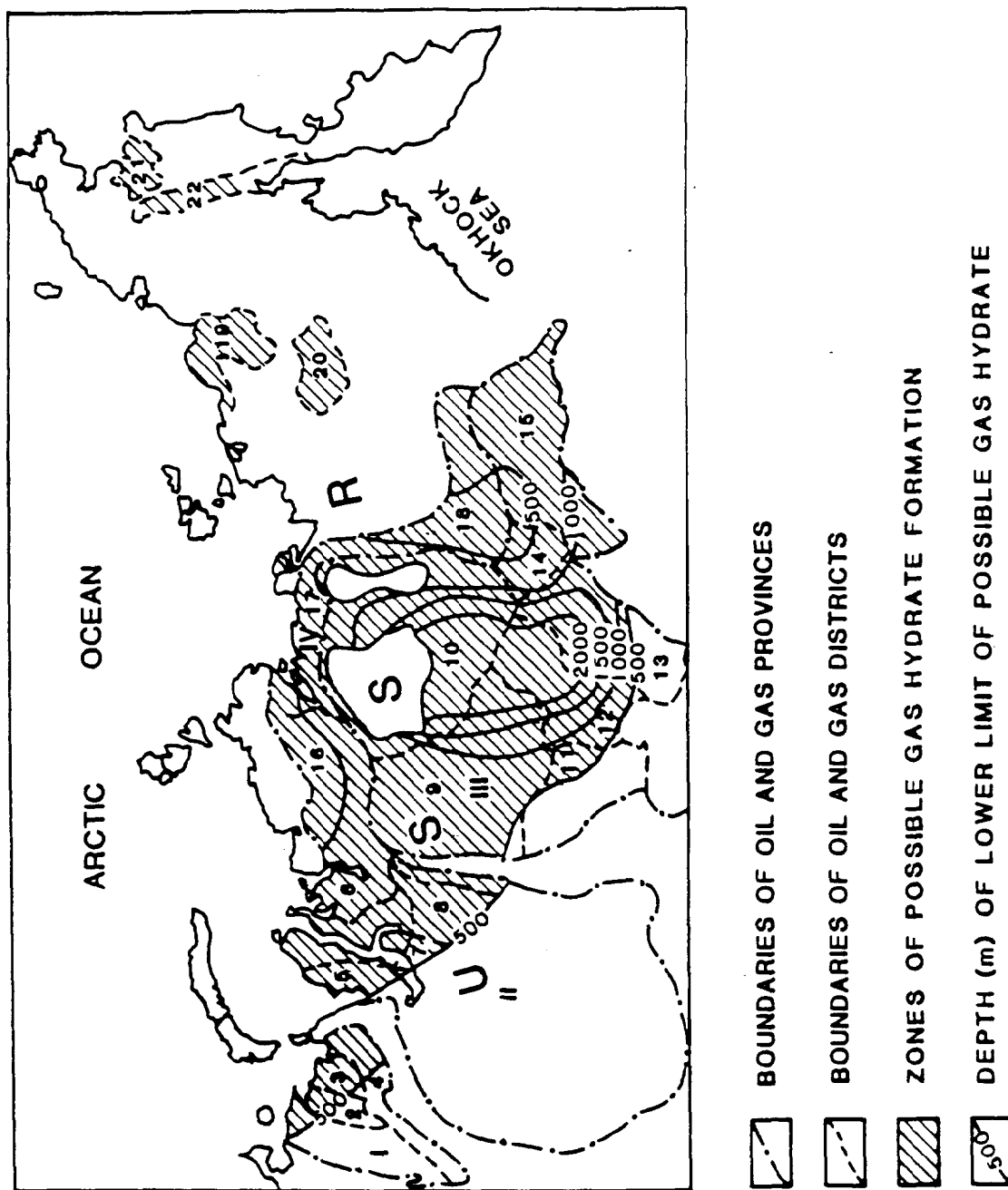


Figure 33. DISTRIBUTION OF POTENTIAL GAS HYDRATES  
IN CONTINENTAL AREAS OF THE USSR  
After Barkan and Voronov (1982)

**LEGEND TO FIGURE 33, ZONES OF POSSIBLE GAS HYDRATE  
FORMATION OF OIL AND GAS PROVINCES AND DISTRICTS  
IN THE USSR**

PROVINCES:		DISTRICTS
I	TIMANO-PETCHORSKAYA	1. IZHMA-PETCHORSKII 2. PETCHORO-KALVINSKII 3. KHOREIVER-MOREYOUSKII 4. SEVERO-PREDURALSKII
II	ZAPADNO-SIBIRSKAYA	5. YUZHNO-YAMALSKII 6. GYDANSKII 7. NADIM-PURSKII 8. PUR-TAZOVSKII
III	LENO-TUNGUSKAYA	9. SEVERO-TUNGUSKII 10. ANABARSKII 11. YUZHNO-TUNGUSKII 12. KATANGSKII 13. NEPSKO-BOTUOBINSKII 14. ZAPADNO-ALDANSKII 15. SEVERO-ALDANSKII
IV	KHATANSKO-VILYUISKII	16. YENISEI-KHATANGSKII 17. LENO-ANABARSKII 18. PREDVERKHOYANSKII 19. VILYUISKII
SEPARATE OIL AND GAS DISTRICTS		
		20. MOMO-ZIRANSKII 21. ANADYRSKO-BERINGOVOMORSKII 22. PIENZHIWSKO-PUSTORETSKII



TABLE 14.

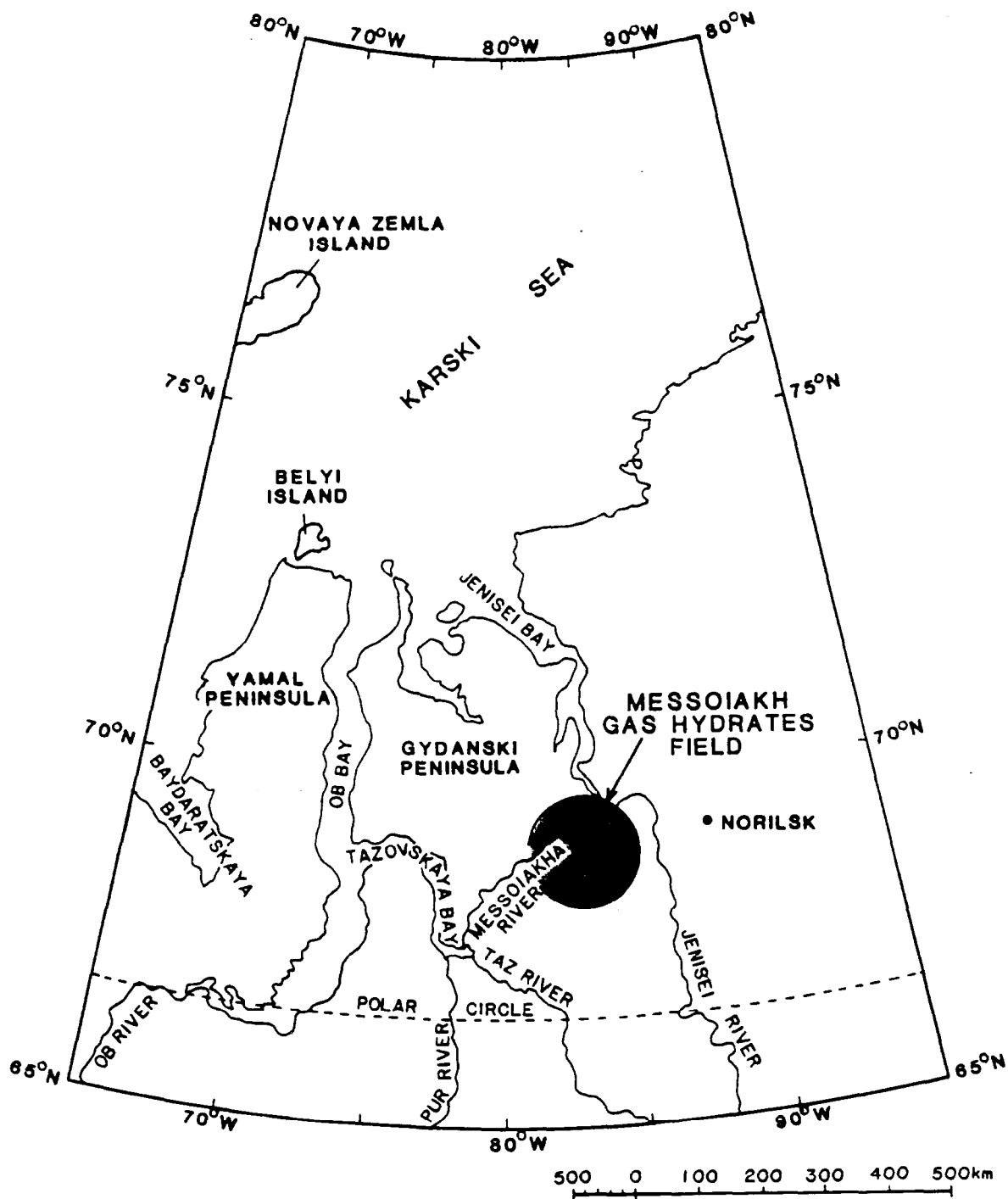
THICKNESS OF PERMAFROST AND DEPTH INTERVALS OF GAS HYDRATE ZONES IN SOME SIBERIAN AREAS. After Makogon (1974).

Area	Thickness of permafrost zone m	Depth interval of hydrate formation	
		from m	to m
Yst' Birlok	150	100	425
Solian	200	100	700
Olekmin	100	150	2000
Namanin	85	200	1650
Russko-Rechen	90	100	1100
Ilychir	100	100	500
Sredne-Botuobin	620	100	2000
Amgin	150	100	1000
Markhin	1440	100	2200
Dzharzhn	-	450	800
Bakhynai	-	300	1200
Ust' Vilyui	-	100	370
Oloi	-	100	570
Bergin	-	200	350
Nizhne-Vilyui	-	250	1120
Nedzhelin	-	270	900
Mastakh	-	250	900
Tolon	-	320	800
Sredne-Vilyui	-	370	1100
Vilyui	-	330	1180
Nam	-	300	850

TABLE 15.

THICKNESS OF PERMAFROST AND LOWER DEPTH LIMIT OF THE HYDRATE ZONE IN SOME AREAS OF NORTH AMERICA. After Makogon (1974).

Deposit	Thickness of permafrost zone, m	Lower limit of gas hydrate, m
Cape Simpson	300	650
Barrow	450	1100
Cape Thomson	380	1500
Resolute	400	800
Prudhoe Bay	650	1200



**Figure 34. MAP SHOWING APPROXIMATE LOCATION OF THE MESSOIAKH GAS HYDRATES FIELD**

close to hydrostatic (i.e. about 7.8 MPa) while the formation varies within 8 - 12°C temperature (Makogon, 1984). The map of heat flow in West Siberia constructed by Nesterov and Kurchikov (1981) reveals that Messoiakhs field is located in the area of about  $1.07 \times 10^{-6} \text{ cal cm}^{-2} \times \text{s}^{-1}$  (Figures 35, 36, 37, 38 and 39).

Production tests in wells of Messoiakhs field proved to be strongly dependent on gas hydrate occurrence (Makogon et al., 1971; Sheshukov et al., 1972; Sheshukov, 1973; Makogon, 1984). Problems related to the hydrates were twofold (Sheshukov et al., 1972).

- a. gas hydrates formed in tested wells due to the "cooling-effect" when tests were conducted with a depressurization of 40 - 50 atm,
- b. tests performed in zones with natural gas hydrates produced significantly lower gas output compared with tests of free gas zones (Table 16).

In order to prevent hydrate formation in wells several techniques were developed in the Soviet Union. These techniques consist of applying significantly lower testing depressurization values (i.e. 2 - 4 atm) and injection of inhibitors (mainly methanol) which lowers the hydrate equilibrium temperature. In the Soviet Union, continuous efforts have been under way toward improvement of these methods by using inhibitors less expensive than methanol (Sumetz, 1974). Recently mixtures of methanol and calcium chloride seem to have gained increasing acceptance. Some data from the wells where mixed inhibitors were used are shown after Sumetz (1974) in Table 17.

Sharp differences in gas yields during testing of certain intervals were concluded to be due to the presence of gas hydrates (Sheshukov, 1972). Indeed measured thermal gradients (Figure 40) and pressure gradients revealed that parts of the Messoiakhs gas deposits are within the thermodynamic regime of gas hydrates (Figure 41). It has also been found that the lower boundary of the gas hydrate zone is close to the 10°C geo-isotherm (Makogon, 1974; Table 18). While the procedure of methanol injection into the wells was causing dissociation of the hydrates, greatly increasing gas yields, significant amounts of slightly saline water (up to 80%) were recovered. At the same time the possibility of water flow from below the gas-water contact was excluded (Sheshukov, 1972). Thus, it was concluded that dissociating gas hydrates could yield the water with abnormally low salinity. These facts provided further confirmation of the gas hydrate presence in the area.

Very little information on gas production from the hydrates of Messoiakhs field has been released. In this context data presented by Makogon (1984) give an overall view on the gas production. His diagrams (Figure 42 and 43) show various aspects of this production, during the 14-year time period. The entire production time has been divided into five stages. In the first stage (curve AB, Figure 42), formation pressure was maintained below hydrate equilibrium value. During the second stage of production (curve BC, Figure 42) observed formation pressure declined less rapidly than had been projected. The smaller pressure decline rate was due to dissociation of gas hydrates in response to the lowered pressure. In Figure 43, this stage is represented by the upper portion of the curve HK. During this stage gas production declined. Further lowering of production (third stage) led to stabilization of the formation pressure (curve CD, Figure 42). At this time the amount of produced gas was equal to the amount of gas released from dissociated hydrates. The fourth stage of the development was a four year long conservation period.

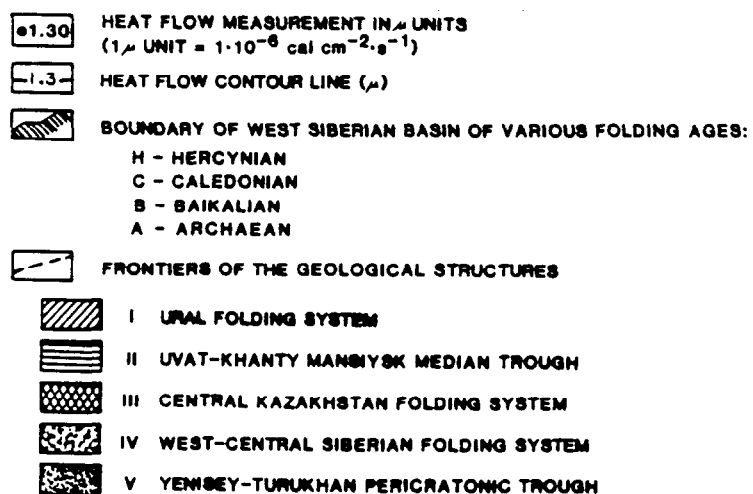
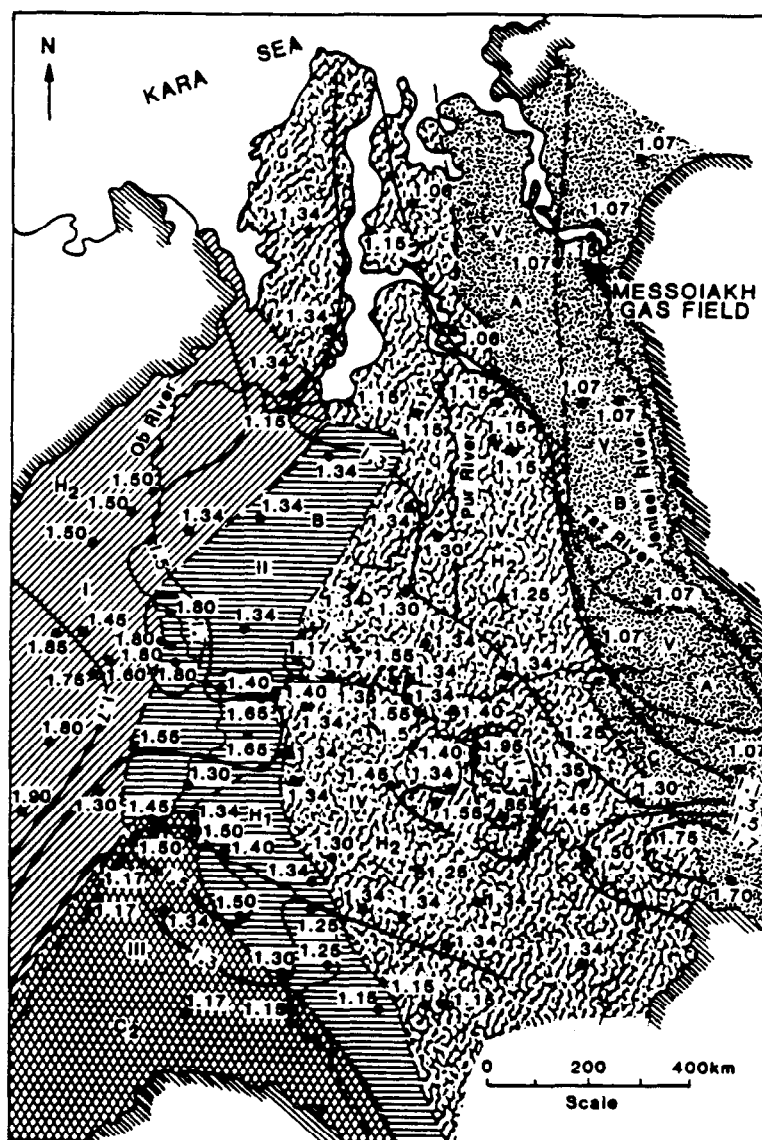
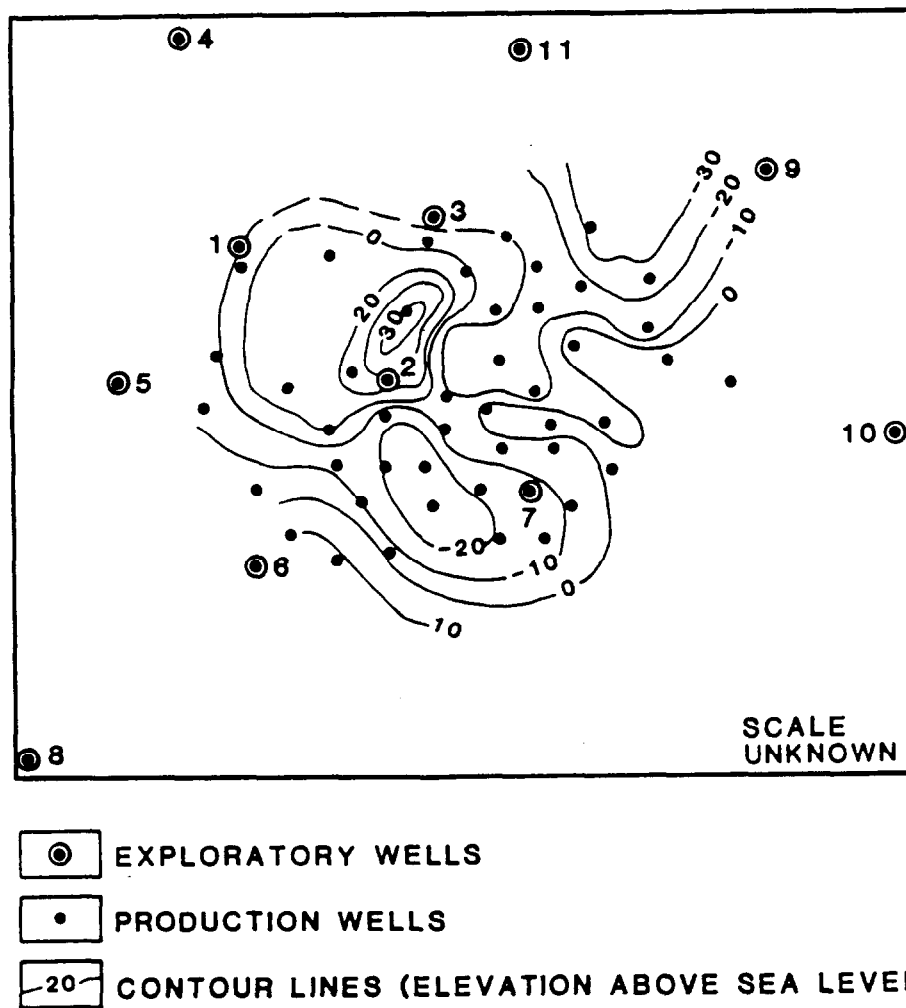


Figure 35. HEAT FLOW IN WEST SIBERIAN PROVINCE

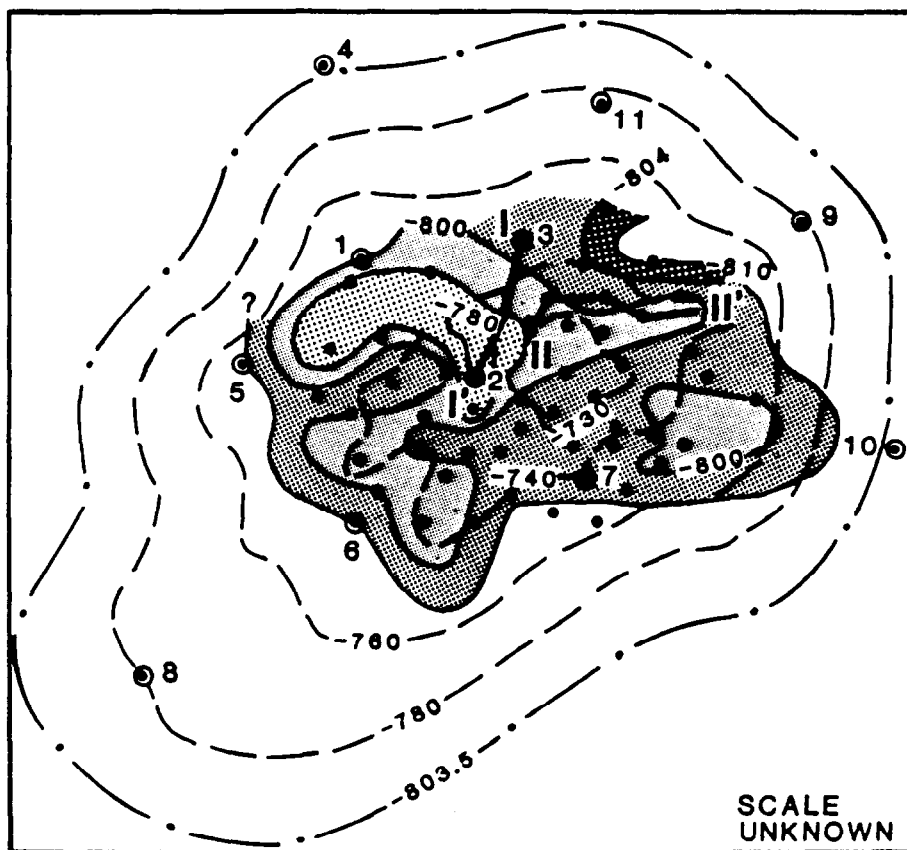
After Nesterov et al. (1981)











**Figure 37. STRUCTURAL MAP OF MIDDLE QUATERNARY HORIZON  
IN THE MESSOIAKH GAS HYDRATES FIELD, BASED  
ON WELL LOGS**

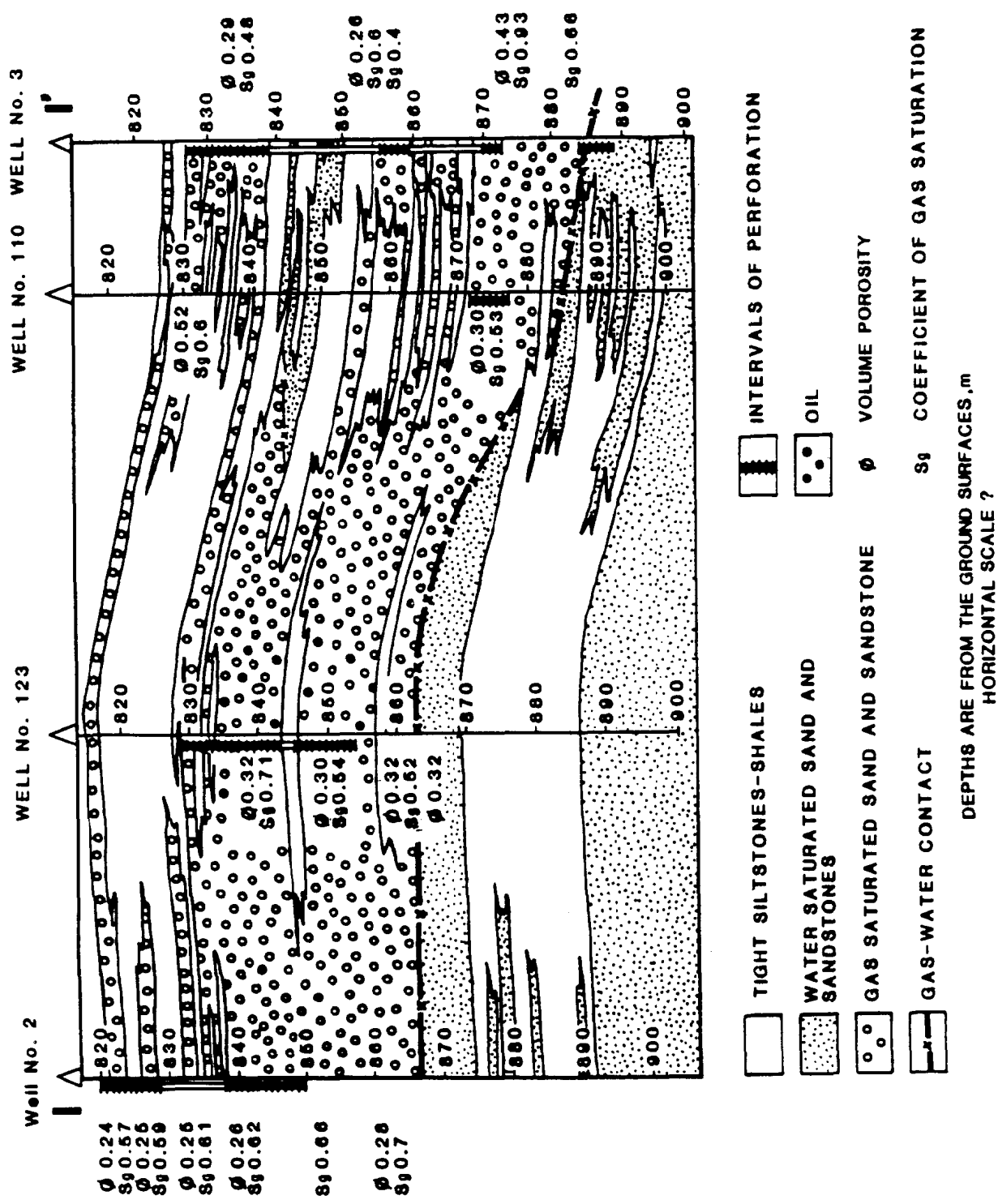
**After Sapir et al (1973)**



-  EXPLORATORY WELLS
-  PRODUCTION WELLS
-  CONTOUR LINES (m) OF GAS-WATER CONTACT
-  CONTOUR LINES (m) OF THE TOP OF GAS PRODUCING STRATA
-  GAS CONTOUR LINE (m)
-  CROSS-SECTION LINE SHOWN IN FIG. 39

**Figure 38. CONTOUR MAP OF THE CENOMANIAN WATER-GAS CONTACT IN THE MESSOIAKH GAS DEPOSITS**

**After Sapir et al. (1973)**



**Figure 39. GEOLOGICAL CROSS-SECTION I-I' SHOWING UPPER CRETACEOUS STRATA IN THE MESSOIAKH GAS HYDRATES FIELD**

After Sapir et al. (1973)



TABLE 16.

TESTED INTERVALS AND GAS FLOWS IN WELLS IN THE MESSOIAXH  
FIELD. After Makogon (1974).

Well number		Intervals of perforation, depths m	Thickness of tested interval m	Gas flow m <sup>3</sup> /day	Gas flow per 1 m of tested interval $\frac{\text{m}^3/\text{day}}{\text{m}}$
Wells with high gas yield	9	789 - 795	6	22	4.4
	5	793 - 803	10	153	15.3
	131	792 - 794	22	285	13
	135	779 - 795	15	99	6.6
	141	764 - 789	23	179	7.8
	134	739 - 791	14.6	238	16.3
	7	746 - 790	16	355	22.2
	142	769 - 795	29	350	12.2
Wells with low gas yield	6	750 - 756	6	3	0.5
	1	745 - 767	20	41	2.05
	113	749 - 780	17.2	55	3.2
	120	746 - 756	8	3	0.4
	146	733 - 785	26.4	35	1.3
	121	746 - 756	8.4	4	0.5
	130	724 - 784	50	108	2
	150	749 - 777	28.2	50	1.8
	151	739 - 749	10	3.5	0.3

TABLE 17.

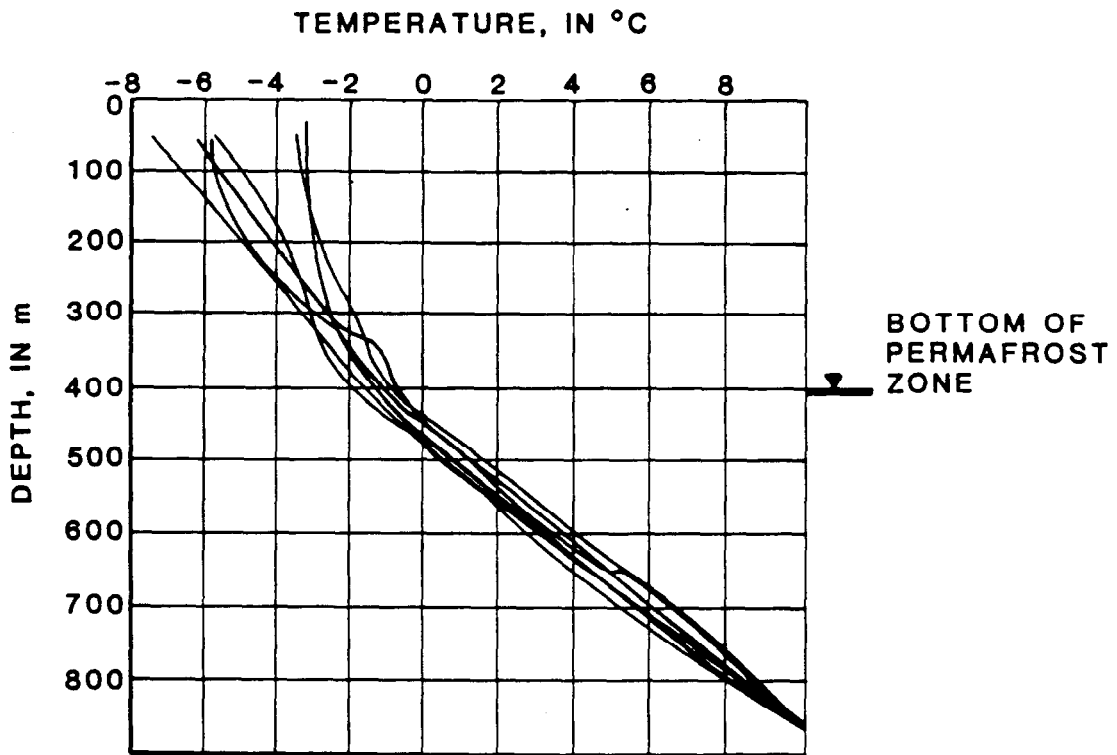
RESULTS OF GAS HYDRATE INHIBITING WITH CHEMICAL TREATMENTS  
IN THE MESSOIAKH FIELD. After Sumetz (1974).

Number of a well	Type of used inhibitor	Method of treatment	Volume of used inhibitor, m <sup>3</sup>	Gas yield before the treatment, 1000 m <sup>3</sup> /day	Gas yield after the treatment, 1000 m <sup>3</sup> /day
129	Methanol (96%)	Injection under pressure using cement-aggregate	3.5	30	150
138	Mixture of: 10% vol. of methanol 90% vol. of 30% CaCl <sub>2</sub>		4.8	200	300
141	Mixture of: 10% vol. of methanol 90% vol. of 30% CaCl <sub>2</sub>		4.8	150	200
139	Mixture of: 10% vol. of methanol 90% vol. of 30% CaCl <sub>2</sub>		2.8	120	180
131	Methanol (50%)	Injection as above with intermittent flushing with gas.	3.0	175	275
2	Methanol (96%)		3.5	Expected results were not achieved.	

TABLE 18.

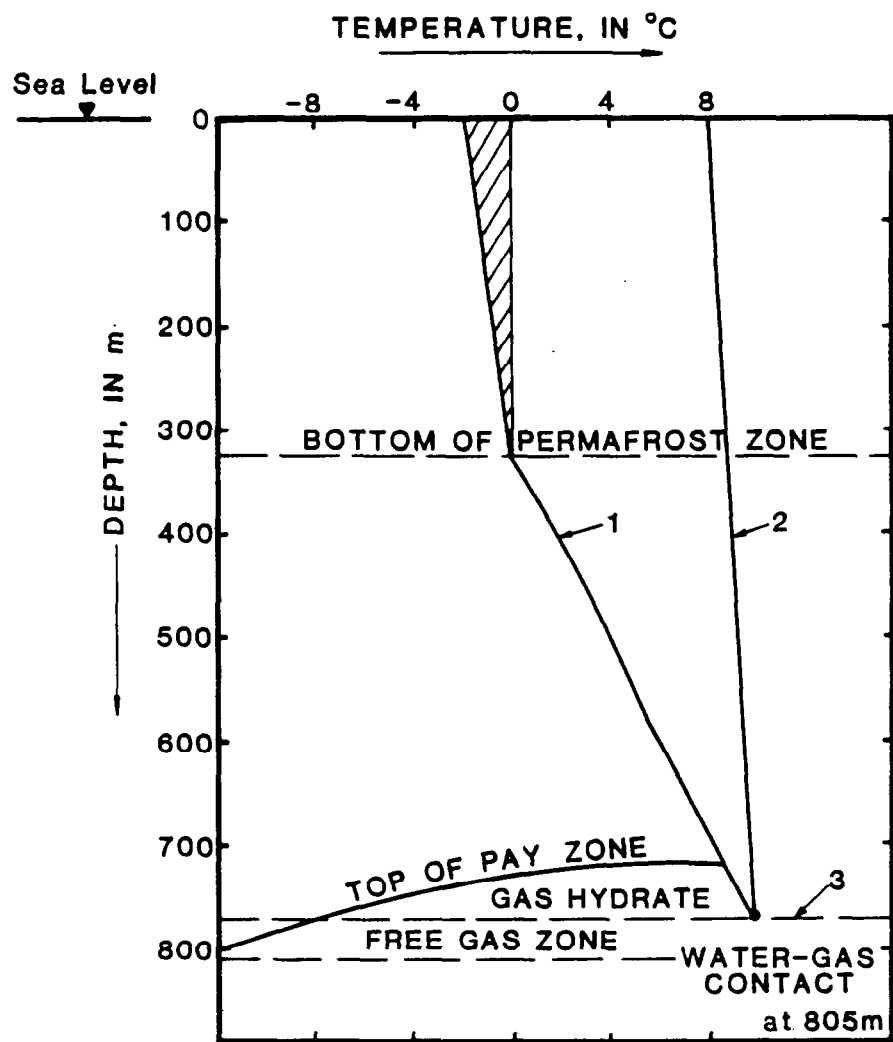
GAS YIELD IN REFERENCE TO THE DEPTH OF PERFORATION  
AND ITS RELATIVE POSITION TO THE ISOTHERM + 10°C IN THE  
MESSOIAKH FIELD. After Makogon (1974).

Well number	Depth of perforation intervals, m	Depth of +10°C. isotherm, m	Distance from perforation holes to +10°C isotherm, m	Free gas flow, 1000 m <sup>3</sup> /day
121	-716-727	-791	+64	26
109	-748-794	-800	+6	133
150	-741-793	-787	-6	413
195	-779-795	-766	-29	626
131	-771-793	-734	-59	1000



**Figure 40. THERMOGRAMS FROM SOME WELLS  
OF THE MESSOIAKH GAS FIELD**

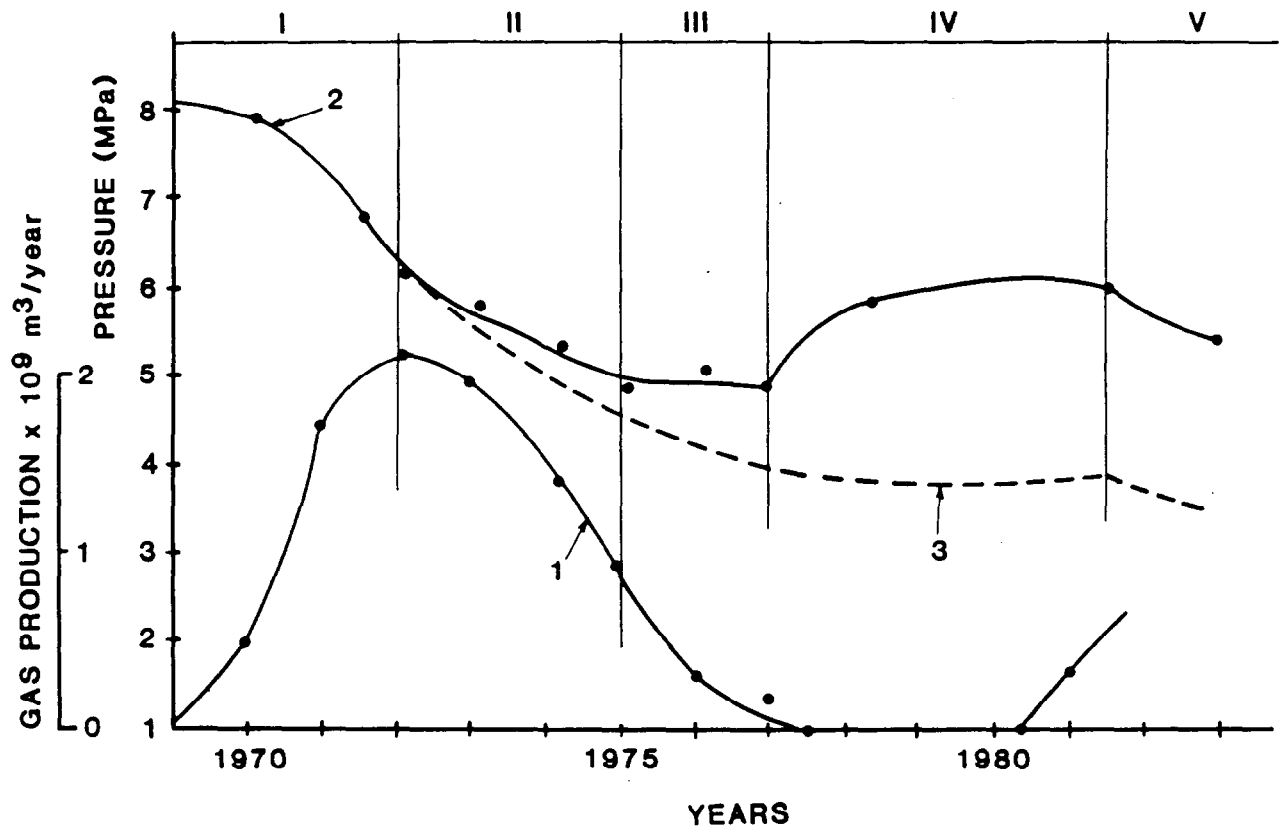
**After Makogon (1974)**



- 1 - CURVE OF STABILIZED FORMATION TEMPERATURES
- 2 - EQUILIBRIUM TEMPERATURES FOR GAS HYDRATE FORMATION
- 3 - LOWER BOUNDARY OF GAS HYDRATE ZONE

**Figure 41. CONDITIONS OF GAS HYDRATE FORMATION  
WITHIN THE MESSOIAKH FIELD**

**After Sheshukov et al. (1972)**

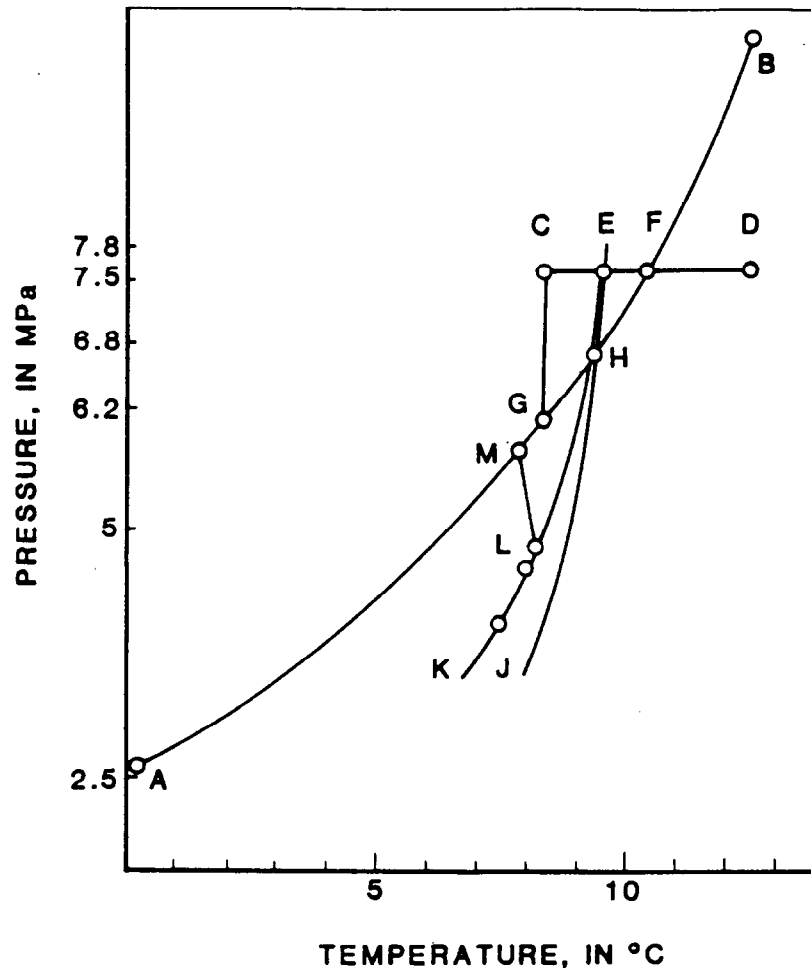


- 1 - ANNUAL GAS PRODUCTION
- 2 - AVERAGE FORMATION PRESSURE
- 3 - PROJECTED FORMATION PRESSURE

- I - GAS MAINLY PRODUCED FROM THE LOWER FREE GAS DEPOSIT
- II - BEGINING OF PRODUCTION FROM THE HYDRATE ZONE
- III - PRODUCED GAS VOLUME EQUALS THE AMOUNT OF GAS DISSOCIATED FROM HYDRATES
- IV - GAS PRODUCTION CEASED FOR REBUILD OF PRESSURE. FORMATION PRESSURE INCREASED AS A RESULT OF GAS HYDRATE DISSOCIATION
- V - RESUMPTION OF GAS PRODUCTION

**Figure 42. CHANGES OF PRODUCTION PARAMETERS FROM THE MESSOIAKH GAS DEPOSIT**

**After Makogon (1984)**



- AB - EQUILIBRIUM CURVE OF HYDRATE FORMATION IN THE GEOLOGICAL ENVIRONMENT
- C - TEMPERATURE IN THE TOP OF THE GAS HYDRATE ZONE
- D - TEMPERATURE AT WATER-GAS CONTACT
- E - AVERAGE TEMPERATURE OF THE GAS HYDRATE ZONE
- F - TEMPERATURE IN THE CONTACT BETWEEN THE FREE GAS AND GAS HYDRATES ZONE
- EFJ - CHANGE OF THE FORMATION TEMPERATURE WITHOUT CONTRIBUTION OF THE HYDRATES DISSOCIATION
- EFK - CHANGE OF THE FORMATION TEMPERATURE WITH THE HYDRATE DISSOCIATION
- G - MINIMUM PRESSURE OF STABILIZED HYDRATE IN A STRATA
- H - PRESSURE AT WHICH THE HYDRATE START TO DISSOCIATE FOR THE AVERAGE TEMPERATURE IN ZONE OF THEIR OCCURRENCE

**Figure 43. THERMODYNAMIC CHARACTERISTICS OF THE MESSOIAKH GAS HYDRATE DEPOSIT**

After Makogon (1984)

Gas production was ceased and the process of hydrate decomposition continued throughout 1981 until the formation pressure reached the equilibrium level. According to Makogon (1984), during the entire time of the development, the water-gas contact remained at the same depth.

### **Marine Gas Hydrates**

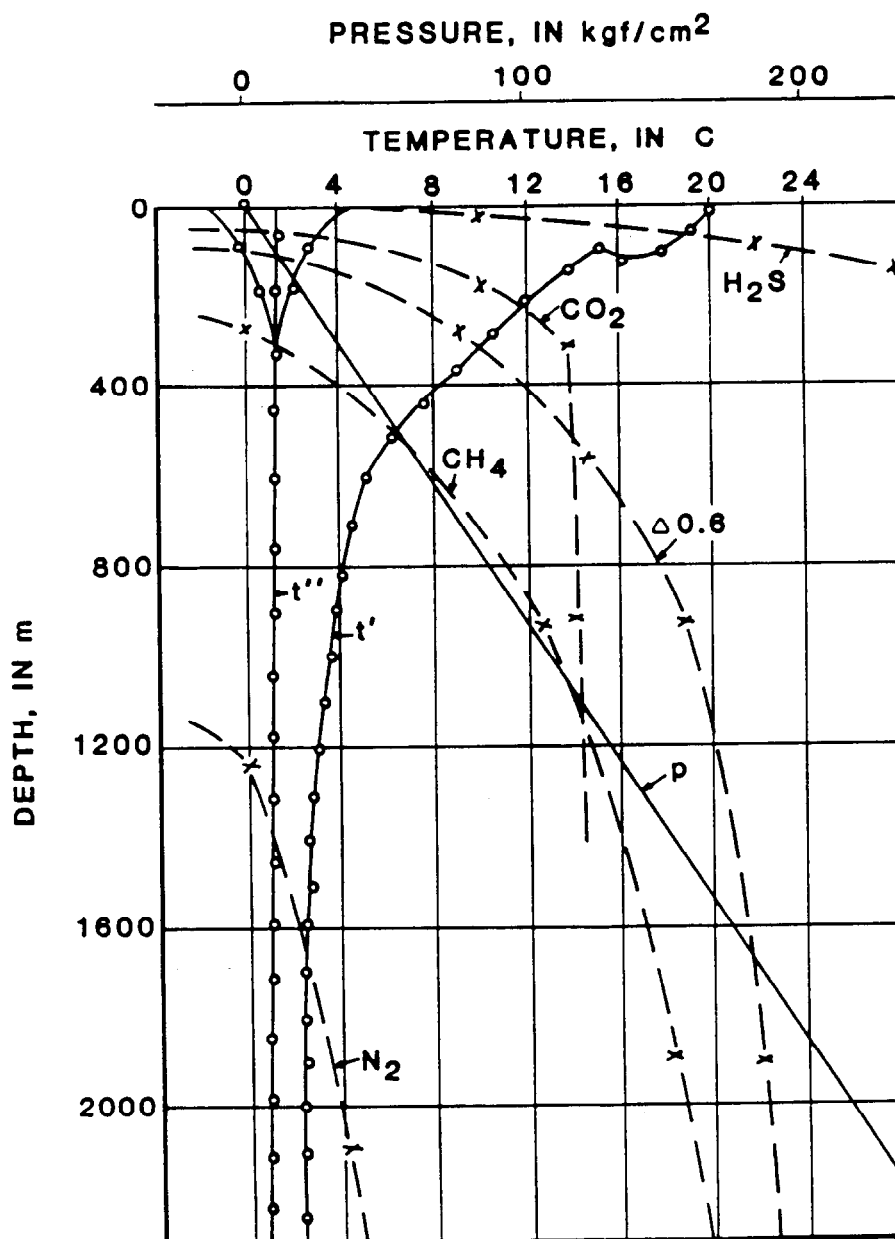
Russian prognoses on the marine occurrence and distribution have rather general and limited character. They are based on the thermodynamic conditions necessary for the hydrates to form and on oceanographic and general marine geology data (e.g. Cherskii and Tsarev, 1977; Makogon, 1973). A plot for determination of possible marine hydrate occurrence, commonly used by Russian authors, is shown on Figure 44 (Makogon, 1973, 1974; Trofimuk et al., 1973, 1978). According to Trofimuk et al. (1978) the conditions for gas hydrate generation and preservation exist on 90% of the worldwide oceanic area. The same authors stated that the zone of possible marine gas hydrate occurrence starts at depths of 100 - 200 m in polar regions, at 200 - 300 m in regions with moderate climatic conditions and at 400 - 600 m in tropical areas. Makogon (1973) published an example of a marine hydrate distribution along longitude 170°E (Figure 45).

Although some elements of marine gas hydrate formation have been investigated in the Soviet Union (Trofimuk et al., 1980), research programs outlined (Cherskii and Tsarev, 1977) and carried out, no offshore hydrate program comparable to the DSDP's has been found in the Russian literature to date. Cherskii and Tsarev (1977) and Makogon (1974) hinted, however, at finding gas hydrates in a core recovered from a well in the Black Sea area, at station No. 116. The hydrates were found 640 - 810 cm below the sea floor where the water depth was 1,950 m. These authors also mentioned that cores recovered from other locations in Black and Caspian Seas displayed unusual gas bubbling and in some cases frostlike hydrate crystals could be seen in the pore space.

One of the most interesting features of gas hydrates presented in Soviet publications is their occurrence and distribution in transitional zones from continent to marine areas in Arctic regions (Makogon, 1973; Trofimuk et al., 1978). A thick zone of permafrost on the continent thins toward the sea shores bringing the lower boundary of the gas hydrate zone to shallower depths. In offshore areas the hydrate zone reverts to deeper intervals. Thus a natural trap is created assuming that the hydrate zone acts as a seal with free gas accumulating underneath (Figure 46).

### **Effect of Glaciation on Gas Hydrate Formation**

Some Russian authors advocate the role of icecaps in the process of gas hydrate formation (Trofimuk et al., 1979). It has been stated by Trofimuk, Cherskii and Tsarev (1979) that during glacial periods icecaps affect pore fluids through changing regional pressure gradients and thus the transfer of



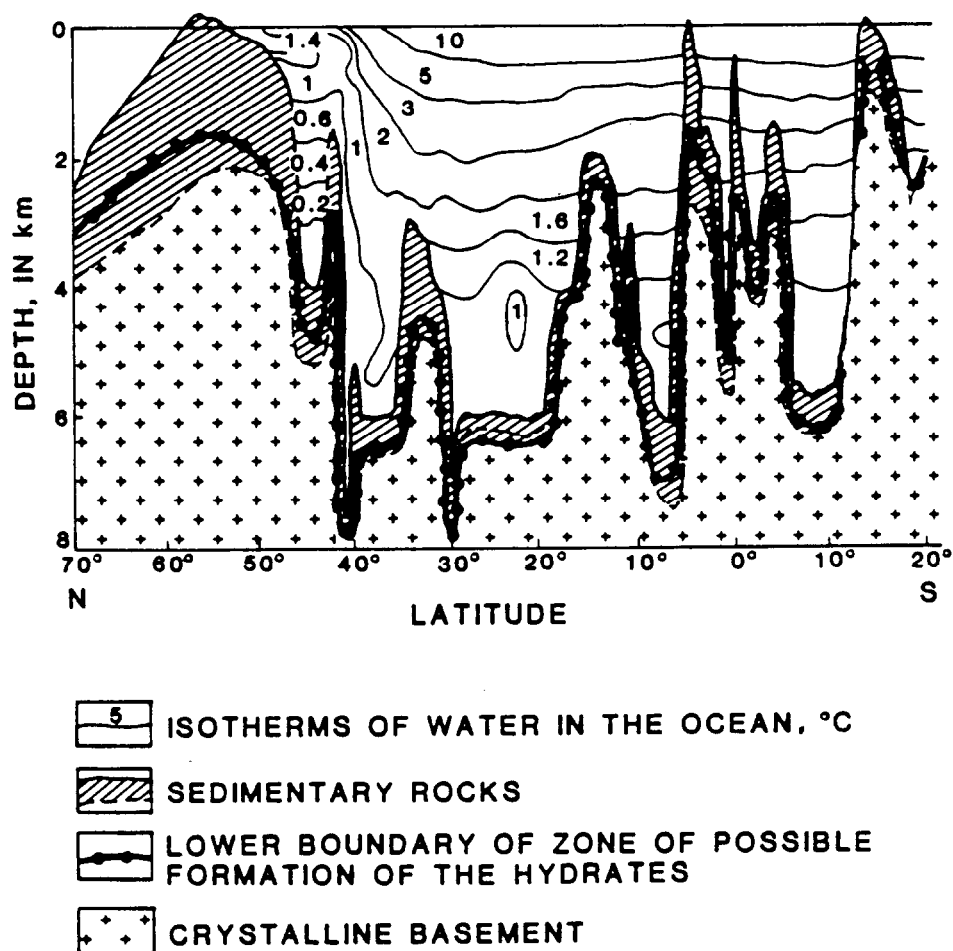
$t', t''$  - changes of the water temperature with ocean depth in subtropics and Arctic areas, respectively

p - formation pressure gradient

**Figure 44. THEORETICAL CURVES FOR DETERMINING THE DEPTH OF THE MARINE GAS HYDRATE FORMATION**

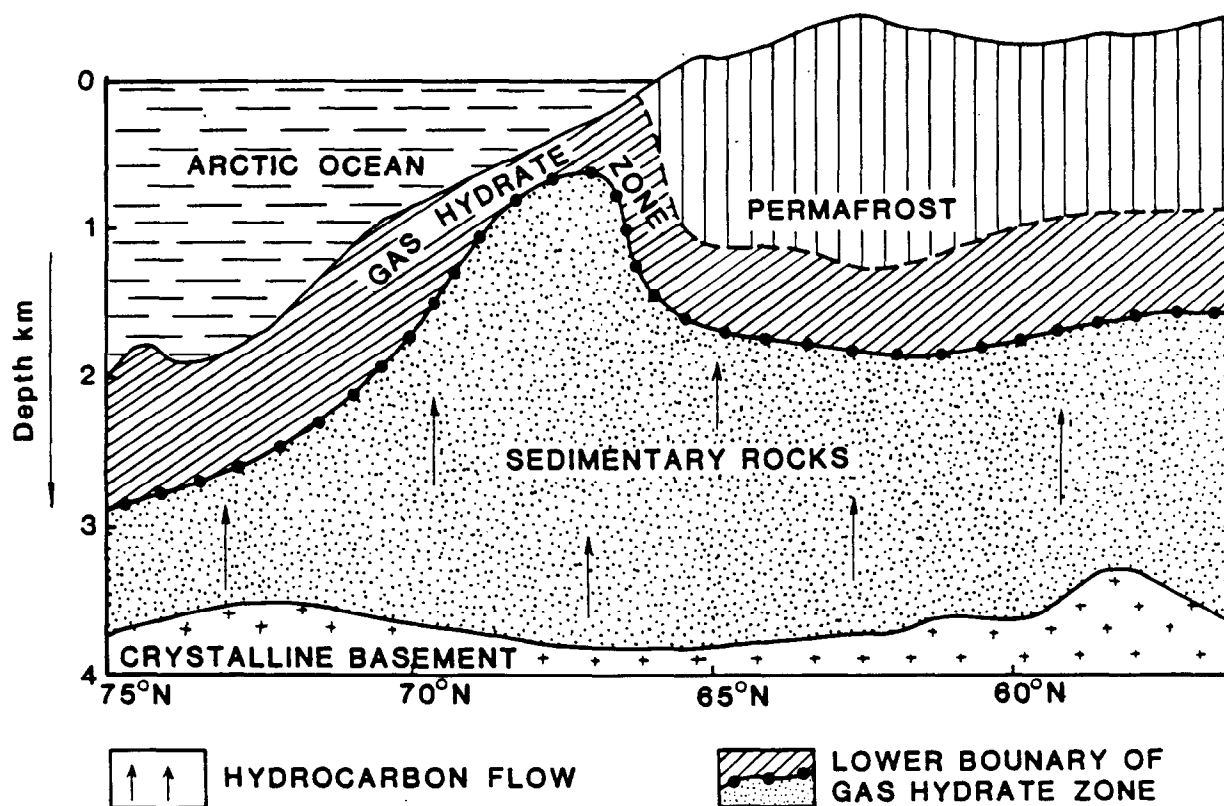
After Makogon (1973)





**Figure 45. OCCURRENCE OF THE NATURAL GAS HYDRATES  
AT THE BOTTOM OF THE PACIFIC OCEAN,  
ALONG LONGITUDE 170°E**

**After Makogon (1973)**



**Figure 46. SCHEMATIC CROSS SECTION WITH GAS HYDRATE ZONE  
ALONG LONGITUDE 175°E AND LATITUDES AS MARKED**

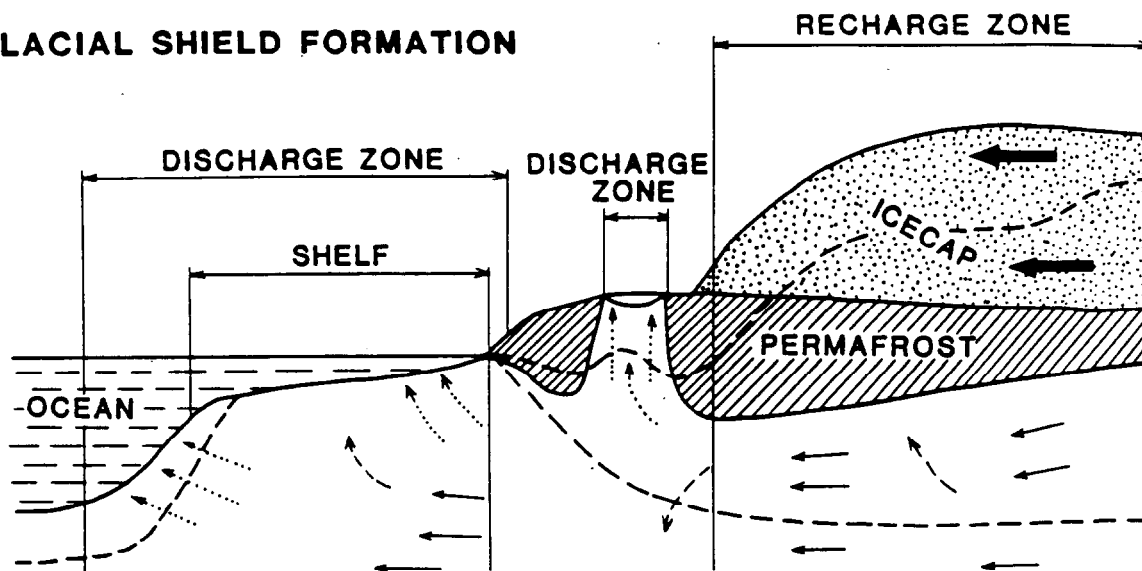
**After Makogon (1973)**

hydrocarbons (primary migration). Tsarev (1976) showed that high formation pressure gradients may result from the movement of icecaps. Thick ice formation may significantly increase geostatic load, thus causing expulsion of the formation fluids. The Russian authors (Trofimuk et al., 1979) pointed at changes of hydrostatic pressure as yet another mechanism which increases the formation pressure gradient. This factor comes into effect when the icecaps move over recharge and discharge zones in areas of artesian type geological structures. The hydrostatic pressure is increased due to the increased column of fluids (Figure 47). Before development of an icecap, climatic cooling was followed by the formation of permafrost. As ice formed and thickened, the temperature at the base of the ice sheet was increasing. As a result the permafrost zone began to thaw. Calculations indicate (Zolotikov, 1977) that during several thousand years the permafrost beneath an icecap can be completely degraded and thus glacial waters are being incorporated into the hydraulic system of artesian reservoirs.

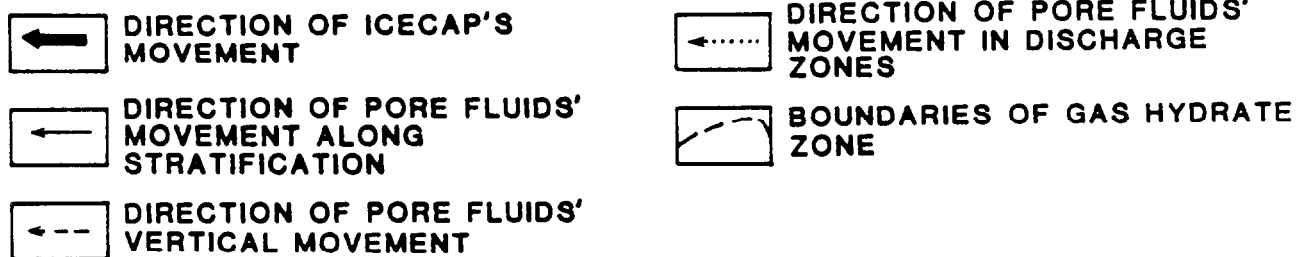
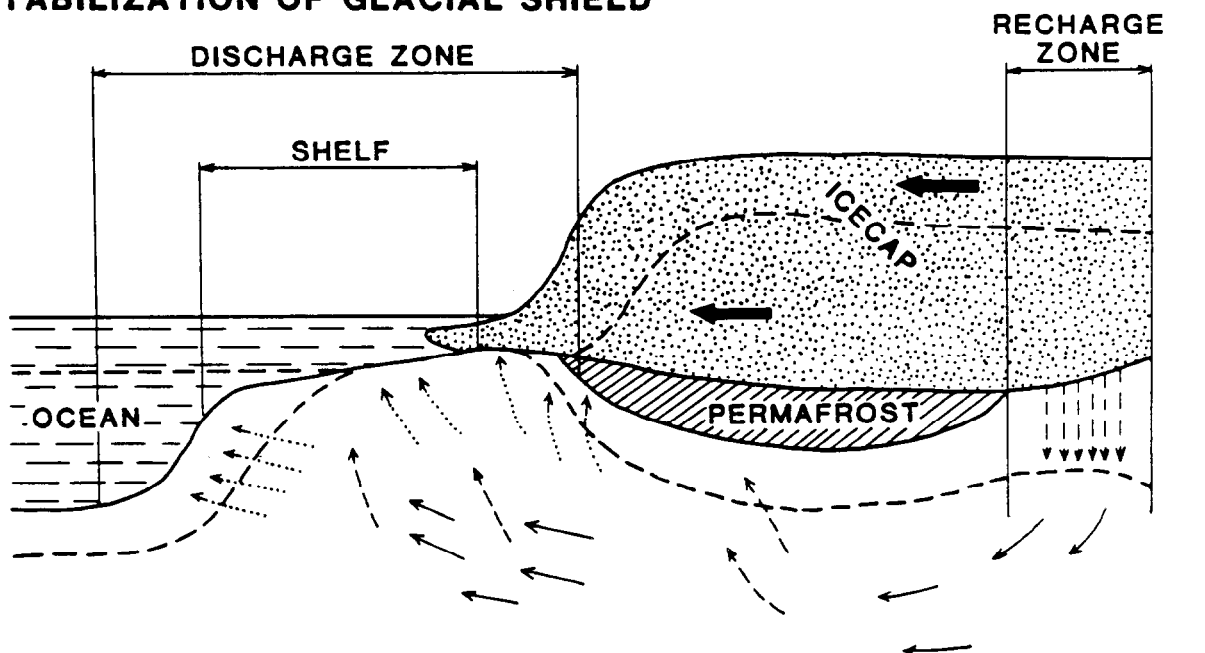
All sudden changes in formation pressure gradients effectively increase primary migration of hydrocarbons. Approaching the hydrate zone, gaseous hydrocarbons become part of this zone in the form of hydrates or remain in the form of dissolved or free gas (Figure 47; Trofimuk et al., 1979). Thickness of the hydrate zone may vary with the thermal regime causing expansion or shrinkage of the zone (Figure 47).

According to the Russian scientists, at the present time the described processes are presumably taking place on the Antarctic continent and during the Pleistocene era they occurred over vast glaciated areas of the Earth.

## A. GLACIAL SHIELD FORMATION



## B. STABILIZATION OF GLACIAL SHIELD



**Figure 47. DIAGRAM OF PORE FLUID MOVEMENT:  
DURING GLACIATION PERIODS**

After Trofimuk et al. (1979)

## NATURAL GAS HYDRATE RESERVES

At the present stage of knowledge of gas hydrates, gas resources calculation with acceptable precision is not possible (Barkan and Voronov, 1982). In the opinion of Barkan and Voronov, the kinetics of the gas hydrate formation process are still not adequately known. Also, more data is needed as to the amount of water converted into hydrates under various physical and chemical conditions. Despite these deficiencies several Russian specialists gave their estimates of gas resources in gas hydrates. The estimates of world gas reserves in the hydrates published by Trofimuk et al., (1978) are  $57 \times 10^{12} \text{ m}^3$  in continental areas and  $5$  to  $25 \times 10^{15} \text{ m}^3$  in continental shelves and continental slopes. Russian calculations of gas resources in the marine hydrates are based on a relatively small amount of factual data (Cherskii and Tsarev, 1977) as to the geometry of gas hydrate deposits, gas saturation, etc. which is available.

In the continental areas, problems of calculating gas resources were carefully studied in the Messoiakh and Vilyui fields, the only locations in the world producing gas partially from hydrate deposits. They constitute natural laboratories which help to establish efficient methods of estimating the gas reserves.

The methodology of calculation of gas reserves in the hydrate deposits was given by Makogon (1974). This method seems to have been originated for the situation where part of gas deposits is in hydrate state (e.g. Messoiakh field). In such case Makogon (1974) proposed the following general formula for gas reserves:

$$Q = Q_G + Q_H + Q$$

where:

$$\begin{aligned} Q &= \text{total gas reserves in the field, m}^3 \\ Q_G &= \text{volume of gas in free state, m}^3 \\ Q_H &= \text{volume of gas in hydrates, m}^3 \\ Q &= \text{volume of gas dissolved in formation water, m}^3 \end{aligned}$$

Volume of free gas  $Q_G$  can be determined from the equation:

$$Q_G = V_R m_0 \frac{T}{P T_z} [1 - s_w + s_w (S_H V_H - S_H)].$$

where:

$$\begin{aligned} V_R &= \text{reservoir volume, m} \\ m_0 &= \text{porosity of the producing part of reservoir} \\ P &= \text{pressure of gas bearing formation, kgf/cm}^2 \end{aligned}$$

- $T$  = formation temperature, K  
 $P_0, T_0$  = standard pressure and temperature  
 $z$  = supercompression coefficient of free gas in the deposit  
 $s_w$  = water saturation  
 $S_H$  = part of pore water converted into hydrates  
 $\psi$  = reaction coefficient - (ratio between gas volume in standard conditions o the volume of water in one mole of hydrate)  
 $V_H$  = specific volume of water in the hydrate state in  $m^3/kg$   
 $V_G$  = volume of 1 mole of gas in standard conditions

For gas reserves in hydrates ( $Q_H$ ) Makogon (1974) recommended the formula:

$$Q_H = V_R \times m_\emptyset \times s_w \times S_H \times \psi$$

and for volume of gas dissolved in pore water ( $Q_\lambda$ ):

$$Q_\lambda = V_R m_\emptyset s_w (1 - S_H) \lambda_s$$

where:

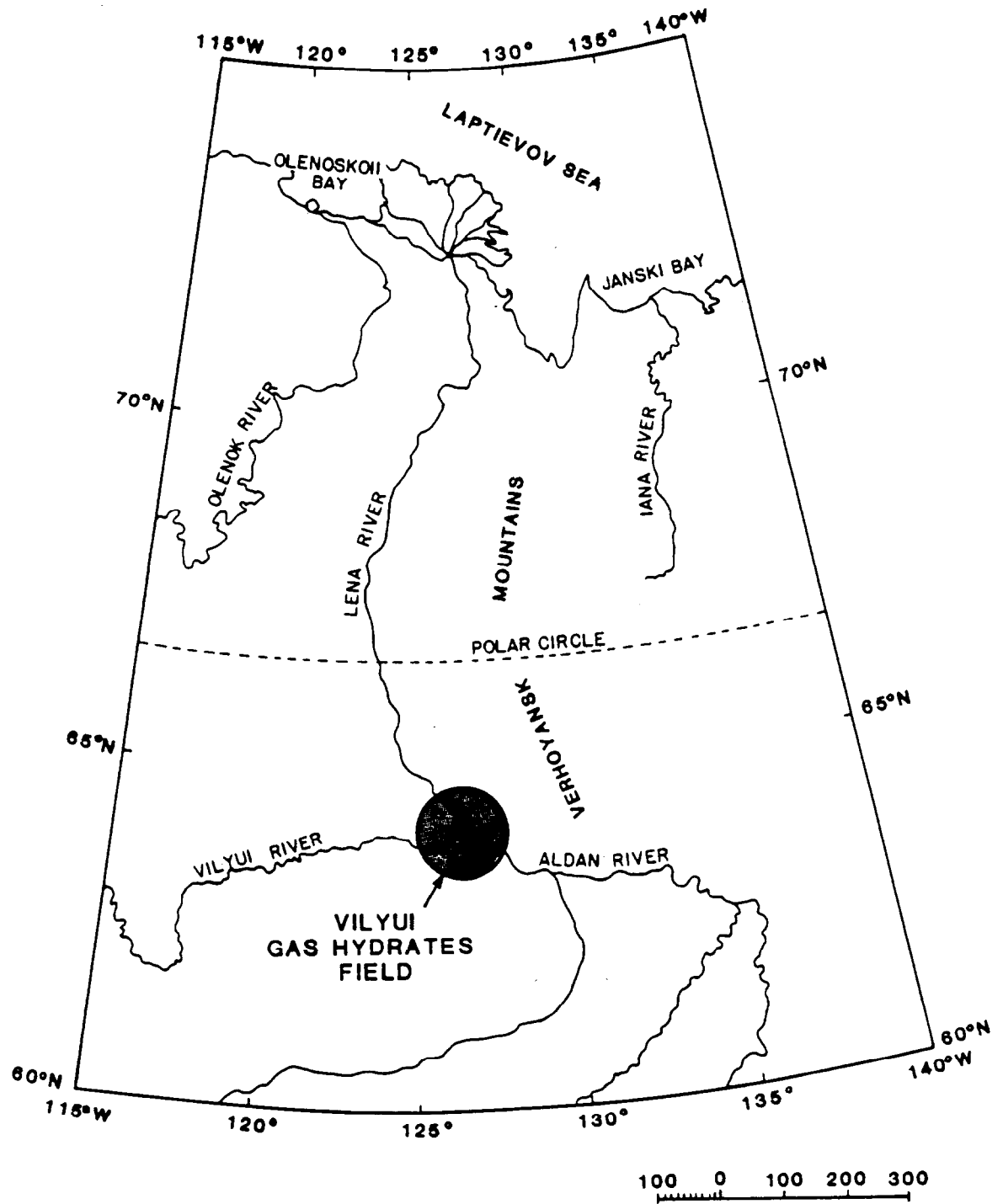
$\lambda_s$  = coefficient of gas solubility in water in presence of hydrates  
 (meanings of the remaining symbols are as above)

The coefficient  $\lambda_s$  depends on gas composition, pressure, and temperature. Its value decreases when molecular weight of the hydrate and pressure in hydrate formation increases. In this method, the amount of water converted into hydrate must be known in order to determine  $s_w$  and  $S_H$ . These data can be obtained experimentally or through tests. Also, porosity and permeability are usually determined through lab core analysis.

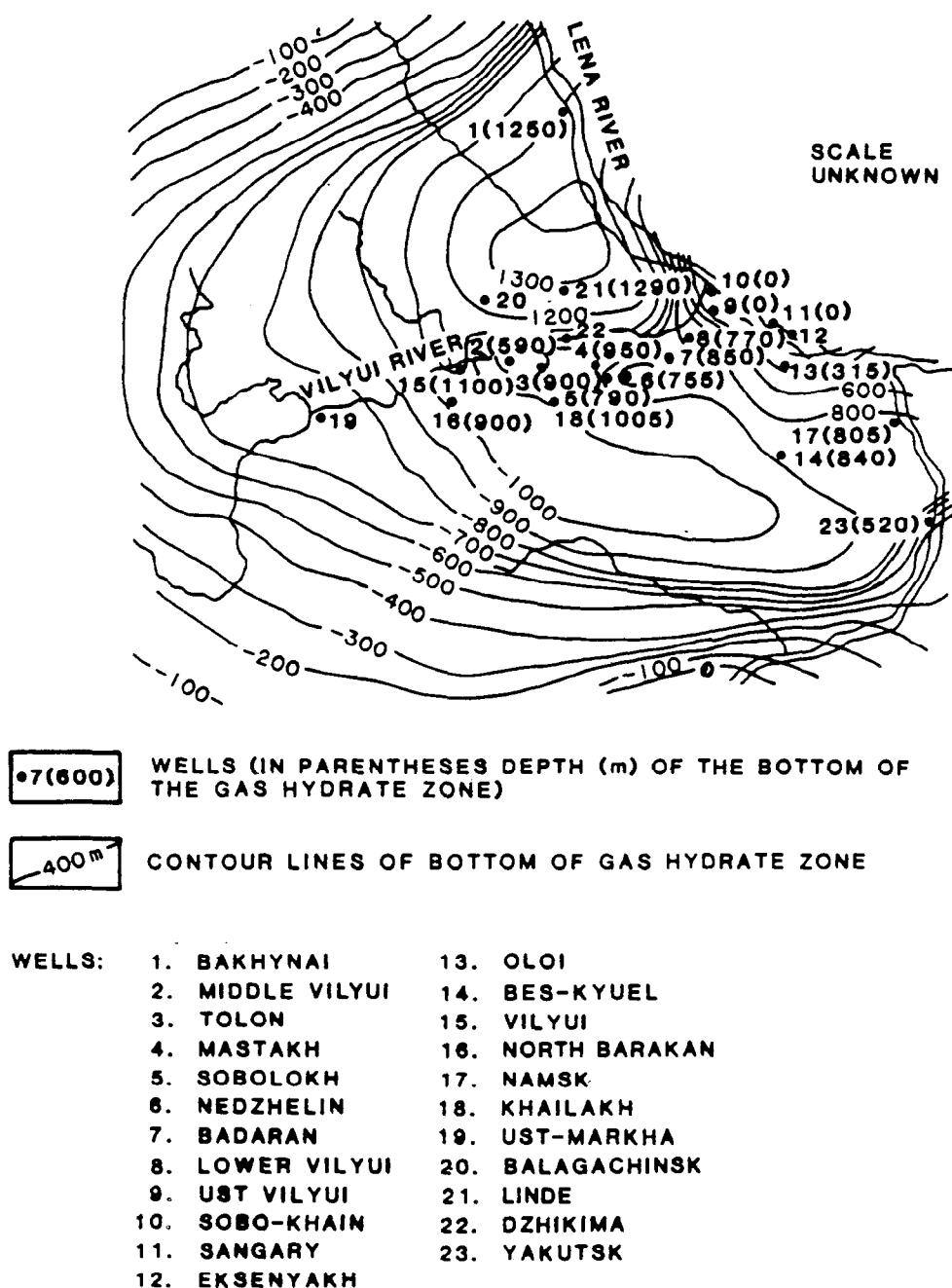
An example of gas reserve estimation in the hydrate zone in Vilyui syncline has been presented by Cherskii and his co-workers (1976; Figure 48). Structural features of the bottom surface of the hydrate zone in the area are shown on Figure 49. Cherskii's estimate was based on the assumption that when the rocks in the hydrate zone were filling with hydrates their permeability was decreasing and gas flow through them gradually diminished. Eventually the strata with hydrates became sealed and a free gas could accumulate underneath the zone.

According to Cherskii et al. (1976), the climatic fluctuations caused the lower hydrate zone to shift vertically. Consequently free gas was either leaving or entering the hydrate zone. As a result of this process the lower section of the hydrate zone was enriched in gas (Figure 50,51) With such assumptions as to the process of hydrate formation, the Russian authors came up with the idea that gas resources ( $Q$ ) within contemporary hydrate zone in Vilyui syncline consist of two segments,  $Q_1$  and  $Q_2$ .  $Q_1$  represents gas deposits enclosed in the hydrate zone at the time of its origin while  $Q_2$  is the part of gas deposits which was incorporated into the hydrate zone during its vertical shifting. Total gas reserves in the hydrate zone can be expressed as follows:

$$Q = Q_1 + Q_2$$



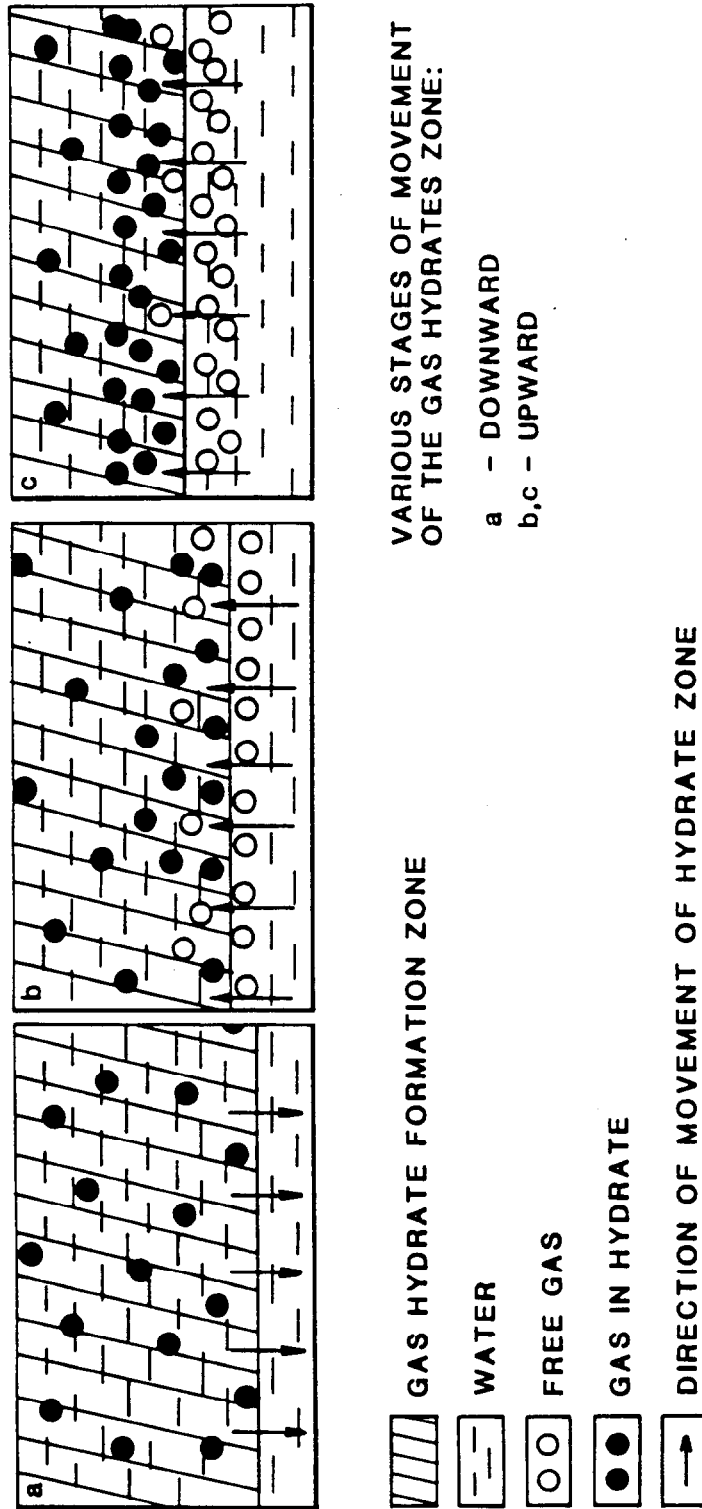
**Figure 48. MAP SHOWING APPROXIMATE LOCATION OF THE VILYUI GAS HYDRATES FIELD**



**Figure 49. CONTOUR MAP OF THE BOTTOM OF GAS HYDRATE ZONE  
IN MESOZOIC STRATA OF THE VILYUI SYNECLISE  
AND ADJACENT REGIONS**

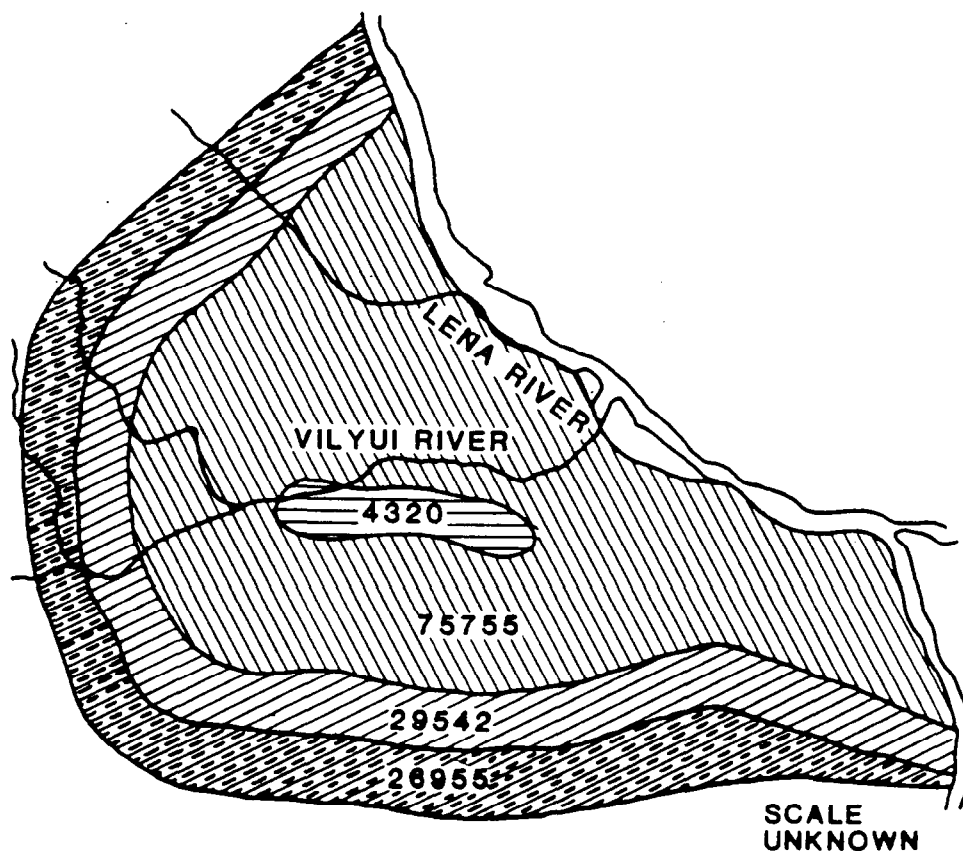
**After Cherskii et al. (1976)**










**Figure 50. EFFECT OF THE MOVEMENT OF GAS HYDRATE ZONE ON NATURAL GAS CONCENTRATION DURING ITS VARIOUS STAGES**

After Cherskii et al. (1976)



# AMPLITUDES OF GAS HYDRATES MIGRATION

-  250 m ( $J_2$ - $J_3$ : M. JURASSIC - U. JURASSIC)
-  250 m ( $J_3$ -K: U. JURASSIC - CRETACEOUS)
-  300 m ( $J_3$ -K: U. JURASSIC - CRETACEOUS)
-  500 m ( $J_3$ -K: U. JURASSIC - CRETACEOUS)
-  4320 AREA (IN SQ. KILOMETERS)

Note: Amplitudes of the gas hydrate migration represent the maximum thickness of sediment which has been within the gas hydrate stability area

**Figure 51. ZONES WITH EQUAL AMPLITUDE OF GAS HYDRATE MIGRATION IN THE VILYUI SYNECLISE AND ADJACENT AREAS**

After Cherskil et al. (1976)

The values of  $Q_1$  can be calculated using classic volumetric methods as this portion of the gas was originally in non-hydrated strata. For calculating the value of  $Q_2$  the Cherskii et al. (1976) suggested the formula:

$$Q_2 = A \cdot H \cdot k_p (n - nk_r) \cdot S$$

where:

- A = coefficient of gas accumulation resulting from mobility of the hydrate zone
- H = thickness of gas hydrate zone, m
- $k_p$  = effective porosity
- n = gas saturation of the formation water prior to the hydrate formation,  $m^3/m^3$
- $k_r$  = reduction coefficient of the formation water saturation in gas in the hydrate formation zone
- S = distribution area,  $m^2$

Results of the estimate are shown in Table 19. In their calculations Cherskii and his co-workers chose a field area of  $1.4 \times 10^5 \text{ km}^2$ . Reserves Q were calculated to a depth of 1,000 m. The Russian scientists obtained a value of  $Q_1$  equal to  $0.13 \times 10^{12} \text{ m}^3$ ; and, after applying recovery factor 0.5, the gas reserves  $Q_1$  were given as  $0.06 \times 10^{12} \text{ m}^3$ . In the calculations of  $Q_2$  the value of  $A = 0.9$  was used assuming 10% of loss due to gas diffusion during accumulation of the hydrates. The maximum value of  $H = 500 \text{ m}$  is, in the opinion of the authors, a conservative figure in view of some other calculations showing  $H = 700 \text{ meters}$  for the area. Gas saturation value of  $2 \text{ m}^3/\text{m}^3$  was used, based on testing data of K-J (Cretaceous-Jurassic age) horizons from non-producing Bakhynai structure. The accommodated value for reduction coefficient of the formation water saturation in gas,  $K = 2$  is minimum since larger values were obtained during experiments. The obtained value of Q was  $7.17 \times 10^{12} \text{ m}^3$ . According to the authors of the estimate considerable difficulties arise in determining the recovery factor for gas hydrate deposits. The experience from the Messoiakhs gas hydrate deposits is that it can vary from 0.1 to 0.5 depending on the production method. Using the minimum value 0.1 the calculations yielded the value of the recoverable gas reserves Q equal  $0.72 \times 10^{12} \text{ m}^3$  (25 TCF) while the total recoverable reserves in the area proved to be  $0.78 \times 10^{12} \text{ m}^3$  (i.e. 27 TCF; Table 19).

Cherskii's methodology of the gas resources estimation in gas hydrate deposits is based on the theory of gas transfer from water solution to gas hydrates, developed by Makogon. According to this theory (Makogon and Koblova, 1972), gas dissolved in water is transmitted to hydrates due to relatively sharp change of its saturation under certain pressure and temperature conditions. A further increase of pressure does not result in any change of the gas solubility in water.

Barkan and Voronov (1982) strongly disagree with such point of view. They expressed the opinion that the equilibrium of the component (gas) in three phase system gas-water-hydrate takes place only when its fugacity in all phases is equal. This condition implicates another, that under equilibrium conditions water should be saturated with gas according to the pressure of hydrate formation. With the increase of pressure the fugacity of the

dissolved gas will increase and since the hydrate formation pressure is constant at given temperatures, the dissolved gas will be transferred into the hydrates accordingly with the conditions of phase equilibrium. If at given temperature the volatility of dissolved gas is bigger than gas pressure over hydrate, the gas will be transferred from water to hydrate. Its current content in water is determined by the value of pressure of hydrate formation and should be calculated separately at each location (Barkan and Voronov, 1982).

TABLE 19.

PREDICTED NATURAL GAS RESERVES IN THE HYDRATE FORMATION ZONE OF THE VILYUI SYNECLISE.  
After Cherskii et al. (1976).

Conditions of gas accumulation in the hydrate zone	Age of deposits	Zone in Fig. 44	Amount of gas transferred to the hydrate zone from water solution, $m^3/m^3$	Accumulation coefficient, A	Amplitude of the hydrate zone migration, Hm	Quantity of hydrocarbons accumulated per area unit, $m^3/m^2$	Area of the hydrate formation zones, $m^2$	Total quantity of accumulated hydrocarb., $m^3$	Predicted recoverable reserves, $m^3$
Accumulated in presence of the gas hydrate zone	J <sub>2</sub> -K	4	1	0.9	500	67.5	75,755 x 10 <sup>6</sup>	5.17 x 10 <sup>12</sup>	0.51 x 10 <sup>12</sup>
		3	1	0.9	300	40.5	4,320 x 10 <sup>6</sup>	0.17 x 10 <sup>12</sup>	0.02 x 10 <sup>12</sup>
		2	1	0.9	250	33.75	29,542 x 10 <sup>6</sup>	1.0 x 10 <sup>12</sup>	0.1 x 10 <sup>12</sup>
		1	1	0.9	250	33.75	26,955 x 10 <sup>6</sup>	0.9 x 10 <sup>12</sup>	0.09 x 10 <sup>12</sup>
Accumulated before gas hydrate formation	J <sub>2</sub> -K	-	-	-	-	-	140,000 x 10 <sup>6</sup>	0.13 x 10 <sup>12</sup>	0.06 x 10 <sup>12</sup>
Total gas reserves								7.30 x 10 <sup>12</sup>	0.78 x 10 <sup>12</sup>

## DEVELOPMENT OF NATURAL GAS HYDRATE DEPOSITS

Data presented by Russian authors (Makogon, 1974; Trofimuk et al., 1978; and others) indicate that gas hydrates occur on 50% of the USSR territory, and on a quarter of the onshore area and on 320 10 km<sup>2</sup> offshore area worldwide. The very good prospects for very large natural gas reserves trapped in gas hydrate structures induced research into their development. Yet despite some Soviet authors' claims (Trofimuk, Cherskii, Tsarev, 1980) that gas production from the gas hydrate deposits including marine hydrates is feasible at the present level of technology, no definite economically sound technique of gas production has been developed. Other scientists, Barkan and Voronov (1982), expressed an idea that production of gas from hydrate deposits will have to be preceded by major technological breakthroughs before production can start on the industrial scale.

Some ideas on the development of the gas hydrate deposits have been presented by Russian scientists (Makogon, 1974; Cherskii and Tsarev, 1977; Trofimuk et al., 1980). Gas extraction from hydrates requires the conversion of gases from the solid bound state to the free state. This conversion can be accomplished by lowering pressure or increasing temperature to values where the hydrate decomposes, or by injection of substances that promote decomposition of the hydrates into the reservoir. The theoretical principles of gas extraction from hydrate deposits were presented by Makogon (1971, 1974) and Khalikov (1971). The calculations were made for gas filtration in porous environments with the ongoing process of the hydrate dissociation. To solve this problem the authors assumed an analogy between processes being investigated in hydrate strata and thermal conductivity during changes of solid phase volumetric conditions. The latter problem is known in theoretical physics under the name of Stefan's problems.

Significant differences in the structural position of the continental and marine hydrates resulted in various methods being proposed for their development.

### Development of Continental Gas Hydrate Deposits

The continental gas hydrate fields are characterized by deep bedded horizons of indurated rocks containing gas hydrates. The first ideas of dissociating hydrates consisted of energy delivery down the borehole or energy in the form of hot water from the subjacent horizons. It has been estimated that delivering energy to the reservoir from the surface is not economically justified (Trofimuk et al., 1982). Trofimuk and his co-workers (1982)

suggested a more economical alternative of in situ combustion by injecting oxygen or air into a gas hydrate horizon and using part of the released gas to heat up and further dissociate the hydrates.

Several other development methods utilizing natural formation heat have been proposed by Russian scientists. One of them consists of decreasing formation pressure in gas hydrate deposits by removing fluids (Tsarev, 1976). The decrease of pressure causes a decrease of the equilibrium temperature which in turn triggers gas hydrate dissociation. Consequently, the formation temperature decreases and the increased thermal gradient further contributes to the gas hydrate dissociation. The mean value of the natural heat flow in continental areas is  $12.56 \times 10^{-6} \text{ J cm}^{-2} \text{ yr}^{-1}$ .

They also indicated that equilibrium temperature may be decreased by delivering substances to the hydrate zone which readily dissolve gas released from the hydrates, diminishing the partial pressure of the gas above the hydrates. A similar effect on the equilibrium temperature can be achieved by injection of gases such as air which do not readily form hydrates.

Tsarev (1976) and others suggested that hot water from the horizons beneath the gas hydrate zone can be utilized for hydrate dissociation. According to them, sources of water with a temperature above  $50^{\circ}\text{C}$  exist in almost the entire area of predicted hydrate distribution in the USSR and in many other parts of the world. In this method, hot water from the subjacent horizons is fed through the well to the lower boundary of the gas hydrate zone. In order to accelerate the dissociation process the water is also injected to other porous horizons of the hydrate zone. Depending on the values of formation pressure and temperature, the gas can be produced 2 to 4 years after the start of the heating procedures. The gas would be produced from a network of production wells. Investigations made by Trofimuk and his co-workers showed that it is a good practice to use 10 - 25% of the heat from the water to dissociate the hydrates and the remainder for heating up the neighboring formations. Using water at  $70 - 90^{\circ}\text{C}$  the maximum gas yield obtained from gas hydrates from one well was 3,000 - 7,000  $\text{m}^3$  a day (Trofimuk et al., 1980).

### Development of Marine Gas Hydrate Deposits

Technical plans for the development of marine gas hydrate deposits proposed by Soviet scientists include suction dredging of hydrate saturated sediments (Trofimuk et al., 1980). The slurry containing gas, hydrates and sediment would be transported to the surface where the separation of gas would be carried out. The efficiency of this method is determined principally by the structural features of the marine hydrate deposit. The upper surfaces of sea bottom sediments with gas hydrates partially filling pore spaces are found from tens of centimeters to more than 200 meters below sea bottom. At the same time major producing zones (up to several hundred meters thick) are located below the shallow hydrate zones (Cherskii and Tsarev, 1977). Thus gas hydrate development requires removal of the upper layers of sediments devoid of the hydrates, the excavation of the sediment poorly saturated with hydrates, and development of the producing horizons at depths of tens and

hundreds of meters from the sea bottom. According to Cherskii and Tsarev (1977), numerous studies showed that the sediments to 1 km of depth below sea bottom are weakly compacted and for practical purposes uncemented; maximum shear resistance values do not exceed 0.2 MPa. In this situation rapid excavation of large volumes of sediments containing gas hydrates should be a relatively easy task (Trofimuk et al., 1980). The same authors presented an example of the gas recovery from 1 m<sup>3</sup> of the sediment covering the main producing hydrate deposits. The assumed gas content in this unit volume was 15 m<sup>3</sup> or up to 100 kg of hydrates. The transportation of the solid particles in slurry from the sea bottom to the surface requires that the weight ratio of water to solids be 10:1. Since in the example 1 m<sup>3</sup> of sediment with porosity of 40% contains 310 kg of water, 100 kg of hydrates and 1,200 kg of other solid materials, 11,690 kg of water is to be used for making the slurry out of the sediment (i.e. 1,200 x 10 - 310). The heat capacity of the materials forming 1 m<sup>3</sup> of the slurry is 52,140 KJ/°C (i.e. 1,256 KJ/°C - solid materials; 49,000 KJ/°C - water added in the slurry preparation). On the other hand, Trofimuk and his coauthors stated that about 38,000 KJ/°C is required to decompose 100 kg of hydrates which corresponds to the decrease of the slurry temperature by 0.8°C. Simple consequence of this fact is that all gas can be released from clathrates without causing significant cooling of the slurry, allowing the slurry to be used as a heat carrier. The process of releasing gas from the hydrates and keeping it dissolved in the slurry depends on equilibrium pressure of the gas over the hydrates. Equilibrium pressure in turn would be determined by the temperature of the slurry. According to Trofimuk et al. (1980) gas from the hydrate deposits will be produced from depths greater than 1,500 m where the pressure values exceed 15 MPa. At this depth the partial pressure of the gas over its solution in the slurry will be 5 MPa. The ratio of gas to water in the slurry will be 15:12 assuming 15 m<sup>3</sup> gas content in 1 m<sup>3</sup> of hydrate bearing sediment. Trofimuk et al. (1980) indicated that an equilibrium methane pressure of 5 MPa over the hydrates in the slurry corresponds to the temperature 7°C. Therefore the temperature of the liquid phase fed to the system should be maintained at 6 - 9°C. At that temperature Trofimuk and his co-workers predict that all gas obtained from hydrates would be dissolved in the slurry eliminating the complex operation of hydrate and sediment separation. The separation of the gas from the slurry would be accomplished at the surface.

Calculated energy needed for the development of gas hydrate deposits according to the plan outlined above would be as follows (Trofimuk et al., 1980):

1. Disturbance of 1 m of the sediments (assumed to be the same as for cemented rocks),

$$E_{\text{Disturbance}} = 1.05 \times 10^3 \text{ kJ/m}^3$$

Assuming 50% of the installations efficiency the corrected value of  $E_{\text{Disturbance}}$  will be:

$$E_{\text{Disturbance}}^{\text{Corrected}} = 2.1 \times 10^3 \text{ kJ/m}^3$$



2. Energy of dissociation of 100 kg of hydrates from 1 m<sup>3</sup> of sediment.

$$E_{\text{Dissociation}} = 42 \times 10^3 \text{ kJ/m}^3$$

After including heat losses in the pipeline

$$E_{\text{Dissociation Corrected}} = 43.5 \times 10^3 \text{ kJ/m}^3$$

3. Energy for lifting 1.2 ton of solid materials requires 24 kW hr or 86,400 kJ/m<sup>3</sup>, assuming that lifting 1 ton of sediment from an ocean depth of 5 km requires 15 - 30 kW hr.
4. Energy needed for solution of 15 m<sup>3</sup> of methane,

$$E = 42,000 \text{ kJ/m}$$

The total energy requirement for the process would be 172,500 kW per 1 m<sup>3</sup> of the sediment which equals 31% of heat of combustion of 15 m<sup>3</sup> of gas (i.e. 565,000 kJ) assumed in the calculations.

Estimated costs of gas production are quite high, \$86 to \$98 per 1,000 m<sup>3</sup> (in 1964 dollar value; Trofimuk et al., 1980). The above presented figures were obtained with assumption of low gas content in the hydrate. Development of the major producing hydrate zones should yield much higher amounts of gas. In the opinion of the Russian authors, the economic feasibility of such enterprise should be improved because of prospect for finding free gas under the hydrate zones. Also the recovery of other valuable components of the hydrated sediments would further increase the profitability of the development of natural gas hydrate deposits.

## DISCUSSION AND RECAPITULATION

Since discovery of the first natural deposit of gas hydrates in 1967, presently known as the "Messoiaikh Gas Hydrates Field" (Makogon, 1974), some Russian scientific institutes represented by numerous professionals have vigorously embarked on the research and exploration programs concerned with the relatively poorly known, but technically very important, phenomenon as a possible economically viable energy resource.

The most advanced laboratory research programs on gas hydrates were carried out in the Gubkin Petrochemical and Gas Industry Institute, in Moscow. This institute, already in the early phase of gas hydrate study, took the leading role on the USSR level. Important programs in the gas hydrate field were also performed at the Institute of Physical and Engineering Problems of Far North, in Yakutsk. Two other institutions actively participated in the gas hydrate investigation, i.e. All Union Oil and Gas Research Institute, in Moscow, and Institute of Geology and Geophysics, in Novosibirsk.

The review of the bibliography of Russian literature directly relevant to the natural deposits of gas hydrates, revealed the names of over 200 scientists. While there is large number of Russian publications, numerous are repetitive. Some Soviet investigators authored or coauthored many publications (e.g. Makogon, at least 40; Cherskii, 29; Tsarev, 25; Trofimuk, 23). These scientists appear to have worked in the hydrate field for many years. Thus, in the first group of Russian specialists in the gas hydrate field include: Y.F. Makogon, N.V. Cherskii, A.A. Trofimuk, V.P. Tsarev, V.A. Khoroshilov, and V.A. Fomina. Their publications seem to represent major developments, results, and achievements of the Soviet scientists in the gas hydrate field.

All Russian publications directly or indirectly related to natural gas hydrate deposits can be divided into four major categories:

1. the theoretical and laboratory investigations on gas hydrate formation, mainly in the area of kinetics and thermodynamics,
2. natural deposits of hydrocarbon gas hydrates in the Messoiaikh and Vilyui fields,
3. gas hydrates in marine environments,
4. the technical problems and energy resource of gas hydrates.

## The Theoretical and Laboratory Investigations on Gas Hydrate Formation

The results of the theoretical study and experimental investigation carried out by the Russian scientists constitute the major contribution to the knowledge of the gas hydrates field.

With regard to **the structural features of the gas hydrates**, B.A. Nikitin pointed out that they may occur in the solid state (Byk et al., 1980). In the 1950s major structural studies on gas hydrates of various gases were conducted in the USA and Germany. Very important discoveries in this field were made by Claussen, Pauling, Marsch, Müller, and von Stackelberg. They used extensively X-ray and mass spectrometry methods. At the same time there is no evidence of major new results made in the USSR in the field of structural features of gas hydrates. Moreover, reviewed Russian literature suggests that data obtained by Western scientists are being routinely used in the USSR.

The first Russian experiments on the hydrocarbon type of gas hydrates were conducted in the 1960s at Gubkin Petrochemical and Gas Industry Institute in Moscow. The experiments were carried out mainly in the field of the kinetics and the thermodynamic conditions of gas hydrate crystallization (Makogon, 1974). These experiments showed that the process of hydrate crystallization takes place at the water-gas contact. Initially this process requires a significant degree of supercooling. Further, it was discovered that below a certain temperature level, water preserves so called "hydrate structure," which consequently requires much less supercooling to convert it back into the hydrate state. The thermal threshold above which water loses its hydrate structure entirely was found to be 35°C (Makogon, 1974).

During experiments under the conditions of free gas/water interface, attempts were made to establish various kinetic relationships of the gas hydrate crystallization process (Makogon, 1974). The paths and rates of hydrate growth were revealed to a certain degree in a quantitative manner. The Russian researchers (Makogon, 1974) found that at the first stage, hydrates tend to grow along a gas-water interface. Once the entire interface is covered with the hydrate, growth of the volume diffusion type prevails. As the hydrates grow thicker the gas diffusion level drops and proportionally the process of hydrate crystallization slows down (Makogon, 1974).

The introduction of a porous environment into the experiments on hydrocarbon gas hydrates constituted an important step forward in the Russian investigations. These experiments were performed for single as well as for multi-component gases. These experiments helped to reveal that the process of hydrate crystallization in a porous environment requires a more vigorous thermal regime (i.e. greater supercooling) compared with the conditions of free water-gas interface. This is due to the diminished water vapor pressure caused by decrease of the effective capillary pressure as the hydrate formation process progresses. Also in the case of the multi-component gases, it was found that lower temperatures are necessary for hydrate formation than in the case of single component gas with lower molecular weight (Makogon, 1974). These experimental results indicate that the gas components with lower value of vapor pressure form gas hydrates first. At the same time the remaining gas composition is enriched in gases which require lower temperatures to form the hydrate (Figure 14).

The influence of the porous environment on hydrate equilibrium conditions was investigated for various ranges of pressure (Makogon, 1974). Experimental investigations led to the conclusion that in lower pressure ranges this influence is greater. Under the condition where water vapor pressure in the porous space is equal to or greater than the water vapor pressure over the hydrate, the porous medium does not practically change the hydrate equilibrium parameters compared to a free water-gas interface (Makogon, 1974).

One of the main factors in the process of hydrate formation is constant gas availability in the environment. It seems that in this field the Russian investigators have not reached a consensus (Barkan and Voronov, 1982). For a relatively long time the theory proposed by Makogon and Koblova (Makogon et al., 1971) was adopted not only by Russians but also by many scientists worldwide (Claypool and Kaplan, 1974). Makogon and Koblova (ibid.) suggested that solubility of methane in water increases to certain value with the rise of pressure (Figure 7). After reaching this point the methane solubility falls sharply and consequently excessive amounts of gas are released from the solution. This gas may enter the potential gas hydrate formation zone.

Barkan and Voronov (1982) expressed doubts over Makogon and Koblova's theory. In Barkan and Voronov's opinion, gas transfer between various phases (gas-water-hydrate) can only take place when its fugacity is different in at least two phases. Conversely, the equilibrium of the three phase system water-hydrate-gas (i.e. there is no transfer of any component to or from any phase of the system) occurs only when the fugacity of a considered component is equal in all phases. The latter considerations led Barkan and Voronov to the conclusion that at the equilibrium conditions the water should be saturated with gas to its maximum capacity at the pressure required for hydrate formation. With the increase of pressure, the fugacity of the dissolved gas will increase. Consequently, if the fugacity of the dissolved gas at a given temperature exceeds the gas pressure over the hydrate, the gas will migrate from water to hydrate, according to phase equilibrium relationships. In this context the Russian authors (Barkan and Voronov, 1982) suggested that the ultimate content of gas dissolved in water gas which will be transferred into hydrate, must be calculated separately for each individual potential gas hydrate site.

Barkan and Voronov's (1982) studies on water saturated with gas in the same geological environments, inside and outside of gas hydrate zones, and on comparison of the gas fugacity in water versus pressure of hydrate formation, revealed that in the majority of the areas of potential hydrate occurrences, only an insignificant amount of gas dissolved in the formation water was transferred into the hydrates.

**The problems of the entropy and enthalpy** of the hydrocarbon gas hydrates have relatively little representation in the Russian literature. In this field Soviet scientists seem to have adopted classic methods developed by von Stackelberg (1954) and other non-Russian scientists (Jonescu, 1978). Makogon (1974) presented the results of the Russian calculations of the heat of hydrate crystallization and dissociation for gases from Shebelin and Orenburg conventional gas fields, based on these methods.

At the same time the efforts by Byk and Fomina (1971), Makogon (1974), Trofimuk (1978) and others were concentrated on investigations of the phase changes within the water-ice-hydrate system and establishing pressure-temperature equilibrium conditions for hydrates of various gases (see Figures 18, 19, 20, and 23). In this field the applied methods range from statistical mechanics to experiments, from which simple analytical equations have been derived for quick practical use (see p. 59).

The problems of the gas hydrate kinetics and thermodynamic conditions of their formation and stability seem to have been assigned as the priorities in the Russian research programs. However, for effective solution of many problems related to gas hydrates, Russian authors admit that present knowledge in the areas of gas hydrate kinetics and thermodynamics is still insufficient and the certainty of favorable potential for substantial gas hydrate reserves requires further research.

#### **Natural Deposits of Hydrocarbon Gas Hydrates in the Messoikh and Vilyui Fields**

The occurrence of natural deposits of gas hydrates in some of the continental areas of the USSR, already in a very early stage of investigation, had been suggested by Russian scientists (Makogon, 1965). Nonetheless, only for the Messoikh and Vilyui fields have more specific data been published and presented in the Russian literature. All information from both fields of gas hydrates constitute a valuable data source, particularly at the present time, when accumulated theoretical and experimental data needs verification in natural environments.

**Messoikh oil and gas field** was discovered in the early 1960s. The field is located in the northeastern part of western Siberia (Figure 34). Geologically it lies in the Yenisei-Khatung trough. Huge reserves of hydrocarbons had been found in a structural type of trapping system in the Dolgan Sandstone of Albian-Cenomanian age (Sapir et al., 1973; Sheshukov et al., 1972). The Dolgan Sandstone which was found at depths of 800 to 900 m proved to have rare and excellent reservoir parameters (e.g. porosity ranging from 16% to 38% with average value of 25%; permeability is approximately 125 md; see Figure 39).

Shortly after discovery of the Messoikh hydrocarbon deposit, production tests showed abnormally low gas yields from otherwise favorable intervals. The idea of gas hydrate presence in this field provided the best explanation for these unusual conditions (Sheshukov et al., 1972). Indeed, it had been found later that the entire upper section of the reservoir consists of gas hydrates. Measurements of thermal and pressure regimes in the gas hydrate zone of the Messoikh field showed that the zone is within the gas hydrate stability field (Figure 41). After the gas hydrate was taken into account the total gas reserves of the Messoikh field increased from  $18 \times 10^9 \text{ m}^3$  to  $80 \times 10^9 \text{ m}^3$  (Sheshukov et al., 1972).

Subsequently, the Messoikh gas hydrate field had been used as the natural laboratory, particularly in research on gas production techniques. The

applied techniques consisted mostly of depressurization and inhibiting the hydrates mainly with methanol. According to the Russian authors, current efforts in this field are oriented toward using less expensive inhibitors than methanol (Sumetz, 1974). Because of the complex nature of the gas hydrates and lack of information, procedures of inhibiting with full control of the production parameters indicate that efficient methods of gas recovery from the hydrate deposits have not been achieved.

Gas production from the hydrates of the Messoikh field was initiated by inhibiting from the lower boundary of the hydrate zone upwards. In this way the zone of conventional gas deposits had been enlarged by dissociation of the hydrates.

Detailed information on the technical problems encountered by the Russians during gas production from the gas hydrate deposits are still very scarce. However, in 1984 Makogon presented production curves and pressure changes that took place during 1969 through 1982 gas production, from gas hydrates in the Messoikh field (Figure 42). According to this data, the peak of gas production was achieved in 1972, and it amounted to  $2.1 \times 10^9 \text{ m}^3$  (74 MMMCF) per year (200 MMCFD). After 1972 the production dropped to approximately  $0.2 \times 10^9 \text{ m}^3$  (7 MMMCF) in 1977. From the middle of 1978 to 1980 gas production was ceased for the pressure to rebuild. Approximately in May of 1981 gas production was resumed and steadily increased through 1982. Unfortunately, these data are not accompanied by other information such as inhibiting procedures, efficiency, economics, etc.

In the case of the **Vilyui gas hydrate deposit** the amount of published information is smaller compared to the Messoikh field. It has been known that the Vilyui hydrate deposit is similar to Messoikh in the sense of its relationship to the conventional gas deposits. Russian authors chose Vilyui deposits to present their suggested method of calculating gas reserves in the gas hydrate zones (Cherskii et al., 1976). The methods suggested by Makogon, Cherskii, and their co-workers are presented in this report in the chapter entitled "Natural Gas Hydrate Reserves." It must be stated however, that even among Russian scientists there is considerable controversy over the certainty of these methods. The objections stem mainly from differences in points of view on the gas kinetics in three phase system of water-hydrate-gas, which was discussed above (p. 115).

In both of the above mentioned deposits of gas hydrates the pressure-temperature conditions fully conform with the areas of hydrate equilibrium. However, the kinetics of their original formation and further stability have not been fully explained by Russian authors.

On several occasions Russian authors (Cherskii et al., 1976) discuss and support the thesis about vertical movements of the hydrate zones as a result of their expansion or shrinkage. In the opinion of these authors, the major supporting evidence for the gas hydrate zone movement is higher gas concentration observed in the lower sections of the zone.

The Messoikh and Vilyui deposits are good examples of the trapping mechanism for the conventional type of hydrocarbons by the gas hydrate zone. Nevertheless, these examples represent only one of many structural types of hydrocarbon entrapment. Another entrapment system was recently described by the American author Downey (1984). In this case the gas hydrate zone

horizontally traps the tops of the subsurface outcrops and form the impervious seal for the hydrocarbons which otherwise would escape.

**The transition zone** between the continental and marine environments, within the permafrost regions, is also considered favorable for the gas hydrate deposits (Makogon, 1973). The graphical illustrations of such environments are shown in the Figures 46 and 47. In this zone the lower boundary of gas hydrates is shifted upward, creating permeability closure, which under the favorable conditions may trap the conventional accumulations of gas and/or oil.

The review and evaluation of the literature and available data pertaining to the Messoiakh and Vilyui deposits indicate that Russians devoted relatively little attention to the geological factors, which certainly played a vital role in the gas hydrate formation and stability. Thus, the thorough basin analysis with strong consideration of other critical parameters (pressure, temperature, chemistry of the formation water, gas saturation and diffusion coefficients, heavy isotopes, etc.) should help in better understanding of the complex nature of gas hydrates in general and specifically within the permafrost-continental environments. Certainly, this analysis should result in a model which is much needed for more precise determination of gas hydrate formation and stability, the relationship to the conventional type of hydrocarbon deposits, the most applicable exploration methods, production technology, and economics.

### **Gas Hydrates in Marine Environments**

Marine environments are considered highly favorable for gas hydrate formation and preservation. Moreover, some of the Russian authors (Makogon, 1984; Trofimuk et al., 1981) including E.A. Kozlovsky, the Minister of Geology, USSR (see this report, p. 100), assessed the gas hydrates as an enormous potential energy resource. According to Makogon (1984) there are  $15 \times 10^{15} \text{ m}^3$  of natural gas in the world's oceans.

Gas hydrate occurrences and estimated potential gas reserves in marine environments have been based on the thermal and pressure conditions necessary for hydrate formation and stability as well as on generalized assumptions about biogenic gases formed in the sediments in the continental margins, slopes and the oceanic floors (Cherskii and Tsarev, 1977; Trofimuk et al., 1975; Makogon et al., 1973).

Although most of the Russian authors do not preclude participation of the thermogenic gases in the process of marine gas hydrate formation, biogenic methane is perceived as their main gas component. The calculations made by Cherskii and Tsarev (1977) indicate that the amount of generated biogenic gas in various oceanic zones usually exceeds the amount of dispersed gas, thus creating one of the major preliminary conditions for gas hydrate formation.

According to Trofimuk et al. (1983) favorable thermodynamic conditions for gas hydrate accumulation and stability exist in 90% of the world's seas and oceans. The lower boundary of the marine gas hydrates can be defined by thermal gradients and gas hydrate equilibrium curves (Figure 44). It has

been established that temperature of the polar (i.e. Arctic and Antarctic) seas is very close to 0°C, while in the equatorial regions the temperature of the oceanic water is lower than 5°C at a water depth of 1,000 m, and at the depth of 2,000 m the temperature varies between 1 and 3°C (Makogon et al., 1973). Consequently the minimum depths at which gas hydrates can be formed (assuming gas with relative density 0.6) is 120 m for polar seas and 300 m for subtropical oceanic regions (Makogon et al., 1973).

It appears that the prognosis for marine gas hydrates and more reliable assessments await field verifications. In the reviewed literature there is no indication that Russian scientists have carried out special gas hydrate programs comparable to the United States' Deep Sea Drilling Project (DSDP) in the oceanic regions. Marine hydrates were recovered by the Soviet crews in cores from the bottom sediments of the Black Sea (Yefremova and Khizhchenko, 1974; Makogon, 1974) at station 116, where water depth is 1,950 m. The gas hydrates were encountered at the subbottom depth of 6.40 - 8.10 m. The same authors pointed out that several other cores from the Black and Caspian Seas contained frostlike gas hydrate crystals found in freshly broken rocks. Makogon (1974) also stated that gas hydrates were spotted in several cores from the Pacific Ocean. The cores have been recovered from the bottom of the ocean. There were unusual amounts of gas escaping from each of these cores upon their recovery (Makogon, 1974).

Although the gas hydrates reported and recovered from the Black Sea and the Pacific Ocean are very important, the Russian contribution in this achievement is considerably diminished by the withholding of more specific information.

### **Technical Problems and Energy Resources of Gas Hydrates**

Although a large number of the Russian publications pertain to the theoretical studies, laboratory and field tests, the technical problems caused by the gas hydrates, particularly in the man-made facilities (pipelines and others) were the main motive of many of the scientific and engineering investigations. Some of these problems and considerations of gas hydrates as an alternative energy resource are also worthy of special attention.

### **Glaciation and Gas Hydrates**

In spite of larger gas hydrate reserves that are anticipated in the offshore environments (Trofimuk et al., 1980), Russians focus their exploration efforts on the continental regions. Especially in continental environments, gas hydrate deposits are directly related to permafrost.

Apparently, present permafrosts greatly coincide with the regions glaciated during the Pleistocene period (Cherskii et al., 1985). At that time vast areas of the USSR and other parts of the earth were covered with a thick mass of ice. Some of the Russian authors (Trofimuk, Cherskii, Tsarev, 1979) emphasize the importance of glaciation events in the process of gas



hydrate formation. The role of the ice cover movement is considered an important factor which can change formation pressure gradients. When the glacier moves over ground water charge or discharge areas within artesian type hydrogeological conditions, the formation pressure can be affected by increased column of water (i.e. additional hydrostatic pressure; Figure 47). Thick ice cover also increases geostatic pressure, expelling formation fluids.

During the glaciation periods, thickening of the ice sheet causes permafrost underneath to thaw (Tsarev, 1976). As a result, large amounts of water can be supplied to the natural hydraulic system, particularly in artesian type reservoirs.

The above mentioned authors perceive a close relationship between altered hydraulic gradients, generated by glaciation processes, and gas hydrate formation. Under these circumstances, directions and intensity of the primary migration of the hydrocarbons can be changed. Furthermore, in cases when the water containing hydrocarbons will transport them closely to the gas hydrate zone, dissolved hydrocarbons may enter the gas hydrate stability area (Figure 47).

### Gas Reserves in Gas Hydrate Deposits

According to Barkan and Voronov (1982) the calculation of gas reserves in the hydrate state, with acceptable accuracy is premature at the present time. This is due to the gaps in the knowledge of gas hydrate kinetics and difficulties in the calculations of the amount of water transferred into hydrates under various physical and chemical conditions. Therefore, only general evaluation of the gas entrapped in the hydrates is possible.

The most commonly cited figures of gas reserves in gas hydrates obtained by Russian authors are those given by Trofimuk et al. (1981). These authors show  $57 \times 10^{12} \text{ m}^3$  of total gas reserves in the continental deposits (beneath permafrost) and  $5 - 25 \times 10^{15} \text{ m}^3$  in offshore regions of continental margins and slopes.

In the USSR's territory, 50% of gas hydrate reserves are located in the Leno-Vilyui province, 25% in Khatangsko-Vilyui province, and 15% in West Siberia (Barkan and Voronov, 1982; Figure 33). In the northwestern and Kamchatka oil and gas districts the gas hydrate amount is 5%, while according to the same authors, the Timano-Pechoria province contains less than 2% of the entire Russian gas reserves in the gas hydrate state.

The methodology of calculation of gas reserves in gas hydrate deposits was presented by Makogon (1974); Cherskii, Tsarev and Solov'ev (1976); Barkan and Voronov (1982). While Makogon's and Barkan and Voronov's methodologies are generally applied, Cherskii and his co-workers showed and suggested the method used in calculation of the gas reserves in the gas hydrate deposit of the Vilyui Syncline.

All suggested methods are based on the general model (explained hereunder) of gas hydrate deposit formation (Cherskii et al., 1974). Thus it is suggested by Cherskii et al. (1976) that total gas reserves in hydrate deposits be calculated as a sum of gas deposits formed before gas hydrate crystallization and which was then transformed into hydrates and gas which

entered the gas hydrate zone during its further evolution. The second portion of the gas reserves, which enriched the initial gas hydrate zone is thought to be dependent on the mechanism of gas hydrate vertical movements (Figure 50). The movement was caused by the expansion or shrinkage of the gas hydrates in accordance with variation of the thermodynamic regime in the gas hydrate zone.

Lack of consensus among the Russian authors on the dynamics of gas hydrate zone evolution stems from the consideration that the enrichment of hydrates in gas is stimulated by gas transfer from water to the hydrate zone. These processes however, are not fully understood (see discussion in this report, p. 115).

Total gas reserves in the gas hydrate deposit in the Vilyui Syncline, calculated by Cherskii and co-workers amounts to  $7.3 \times 10^{12} \text{ m}^3$  which occurs in the area  $14 \times 10^4 \text{ km}^2$  (Table 21).

Russian evaluation of gas reserves in marine hydrates worldwide were made by Cherskii and Tsarev (1977). Their calculations of generated and dispersed methane in the continental shelves, slopes and oceanic floor showed net  $\text{CH}_4$  accumulations of  $0.07 \times 10^{-11}$ ,  $0.01 \times 10^{-11}$  and  $0.001 \times 10^{-11} \text{ mole} \cdot \text{cm}^2 \cdot \text{s}^{-1}$  in the respective regions. Assuming a time span of the continued sedimentary deposition in these regions as: 1 m.y., 3 m.y. and 80 m.y., the Russian authors found that 4,842, 2,075 and 5,533  $\text{m}^3$  of methane gas was accumulated in 1 m in the above mentioned three geomorphologic regions of the world's oceans. Furthermore, the same authors assumed that the gas hydrate zones can be expected in 10% of the shelves and in the entire areas of continental slopes and oceanic floors respectively. This would amount to potential areal extent of  $26.7 \times 10^5$ ,  $76.5 \times 10^6$  and  $257 \times 10^6 \text{ km}^2$ . Thus, the gas reserves in shelf, slope, and abyssal regions are  $1.3 \times 10^{13} \text{ m}^3$ ,  $1.6 \times 10^{14} \text{ m}^3$  and  $1.4 \times 10^{15} \text{ m}^3$  respectively. The assumption that 1% of the accumulated methane is in hydrate zones led Cherskii and Tsarev to conclude that the total estimated gas reserves in the marine hydrates equals  $15 \times 10^{17} \text{ m}^3$  (Cherskii and Tsarev, 1977).

It was stated previously (p. 100) that these gas reserve calculations are based on various assumptions which impose a lower level of confidence on the evaluation of these gas reserves than the usually more reliable figures used for the calculation. Nevertheless, before any credible figures on gas reserves in the hydrate deposits are produced, much better knowledge of gas hydrate formation is required and has to be verified with more detailed data.

### Development of Natural Gas Deposits

Discoveries of natural gas hydrates in the continental and subsequently in offshore regions brought also the problems of development of a new type of gas deposit. Several Russian authors presented a considerable amount of relevant information and discussions on suggested development methodologies (Makogon, 1971, 1974; Khoroshilov, 1972, 1974; Burmistrov, 1974; Bukhalter, 1974; Karotaev, 1969; Trofimuk, Cherskii, Tsarev, Nikitin, 1982). Makogon (1974) also presented the theoretical principles of the development of natural gas hydrate deposits.

In industrial practice it is obviously important how the gas hydrates will be dissociated and brought up to the ground surface. Besides the technical

feasibility of the gas development methods, equally important is the economic viability of the enterprise.

Great differences between environmental location, geology and other factors of gas hydrates of the continental and marine type deposits also caused consideration of drastically different development techniques for both groups.

### **Continental Gas Hydrates**

The important feature of these deposits is their location in and association with the permafrost regions. In order to convert the gas hydrates into an energy source, they must be dissociated at their stability zone. Russian experience in this field proved that the conversion process and the use of the delivery of the energy from the ground surface to the gas hydrate zone is not economically feasible (Trofimuk et al., 1982). Trofimuk and his co-workers suggested a more efficient alternative. The injection of oxygen or air into the hydrate zone with part of the liberated gas being used to heat up and dissociate the gas hydrate was strongly considered.

The use of natural formation heat has also been recommended by Cherskii, Trofimuk, Tsarev and Nikitin (1982). One of these methods calls for the decrease of the formation pressure in the gas hydrate zone with subsequent hydrate dissociation. In this process, the lowered temperature of the zone causes increase of the natural heat flow, which further dissociates the hydrates. According to the authors the natural heat flow may increase as much as 3 to 5 times. Hot water from the horizons subjacent to the hydrate deposits for their dissociation was proposed by the same authors. According to this plan the hot water should be delivered to the lower boundary of the gas hydrate zone. In order to accelerate the process of hydrate dissociation the authors suggested to inject the hot water into porous sections of the hydrate zone. Using this method the gas production may start 2 to 4 years after the heating procedures are started. After treatment of the gas hydrates with hot brine or water at a temperature of 70 to 90°C, gas production of 3,000 to 7,000 m<sup>3</sup>/day was obtained from one well in an unidentified location (Cherskii et al., 1982).

Gas hydrate inhibiting techniques probably constitute another of the most commonly used methods in the USSR. In these methods certain substances which decrease the stability equilibrium temperature of gas hydrates are delivered to the hydrate zone. The inhibitors readily dissolve and release gas from the hydrate by diminishing the partial pressure in the gas resting above hydrates. In the Soviet Union the most often used inhibitor is methanol (Table 17; Sumetz, 1974). However, scientific efforts are made toward using less expensive inhibitors than methanol. Calcium chloride seems to have gained industrial acceptance (Sumetz, 1974).

### **Marine Gas Hydrates**

The prospects for gas production from the marine hydrates are far more distant than in the case of the continental deposits. However, in the Russian professional literature (Cherskii et al., 1982), there are also suggestions pertaining to gas hydrate recovery from marine environments. The proposed

methods consist of dredging the sediment saturated with hydrates, suction of the sediment-bearing hydrates, degassing remaining hydrates and separation of gas from the water-slurry at the surface facilities. According to Cherskii and his coauthors most of the gas from marine gas hydrate deposits will be produced from depths greater than 1,500 m.

The calculations made by Cherskii and his co-workers indicate that total energy required for processing 1 m<sup>3</sup> of hydrate-bearing sediment equals 172,500 kWh, i.e. 31% energy obtained in combustion of 15 m<sup>3</sup> of gas assumed to be drawn from 1 m of hydrate-bearing sediment. Economic analysis of the gas produced with the use of the method proposed by Cherskii et al. (1982) also showed that costs of such production are quite high, which make these deposits uneconomic. The authors do not preclude, however, the economic viability in the future when the profitability of such enterprises can be increased due to higher energy costs in conjunction with the recovery of other valuable components from the sea bottom sediment.

Although there are voices in the Soviet Union that gas production from gas hydrate deposits is technically possible already at the present time, not only from the continental areas but also from the offshore areas (Trofimuk et al., 1980), some other authors expressed doubts about such opinions. Barkan and Voronov (1982) wrote: "It needs to be stressed that although gas reserves in the hydrate-bearing strata are valuable resources of hydrocarbons, their production on an industrial scale faces significant difficulties. Therefore, the production cannot be anticipated soon. It is possible, however, that after a major technological breakthrough, the wait for gas production from the gas hydrate deposits will be shortened."

### Exploration Methods

The Russian projections of the occurrences of gas hydrate deposits are generally based on thermal, pressure, geological conditions and drilling data. However, despite the fact that at least two gas hydrate deposits were investigated in detail, very little has been published on the exploration methods which have been applied and could be verified in other areas containing gas hydrates. The published materials on the exploration methods for gas hydrates have only general character and have been mostly presented without reference to any known deposits. Generally three groups of exploration methods have been recommended, namely:

- seismic methods
- geochemical methods
- well logging.

### Seismic Methods

According to Trofimuk et al., (1980) these methods can be particularly useful in exploration for marine deposits of gas hydrates. The authors indicate that the best seismic response is generated from the top surface of the gas hydrate zone. In the opinion of Trofimuk and his co-workers, the

base of the hydrate zone has a transitional character, and therefore, it is not well seen in the seismic sections. However, the same authors stated that only under exceptional circumstances (e.g. when the rocks adjacent to the hydrate zone are saturated with gas) can the base of the hydrate zone be detected.

Apparently suggestions by Russian authors pertaining to the use of seismic methods, especially the interpretation of the seismic data, are extremely different from those interpreted by the American authors (Markl, Bryan, Ewing, 1970; Tucholke, Bryan, Ewing, 1977; Buffler and Watkins, 1978; Paul and Dillon, 1981 and others).

Unfortunately, the recommendations of the use and the interpretation methods of seismic data by the Russian authors have not been documented with any graphical materials from field surveys.

### **Geochemical Methods**

Geochemistry is perceived by Trofimuk et al. (1980) as a particularly useful method in exploration for marine gas hydrates. According to the same authors, Trofimuk, Cherskii and Tsarev (1980), relatively shallow occurrence of methane generation and hydrate zones greatly facilitate sampling procedures, permitting collection at the sea bottom.

One of the inherent features of gas hydrates which can be used in geochemical exploration is the unusual gas content of the sediment. Trofimuk et al. (1980) suggests the consideration of this feature of gas hydrates along with conventional geochemical analyses of the sediment and pore fluids.

Not having available the pressure core barrel, which should enable more precise measurement of gas, the Russian authors calculated gas losses in the process of core recovery from bottom sea sediments. The calculations showed that when using ground coring tubes for samplings in a marine hydrate zone, only 250 cm<sup>3</sup> of gas can be recovered (as maximum) from 1,000 cm<sup>3</sup> of sediment, assuming 250 to 700 cm<sup>3</sup> of gas originally in the sediment.

According to the same Russian authors the figures shown above are in full agreement with the results of the analysis of cores recovered from bottom sediments of Lake Baykal and other (undefined) locations which were highly saturated in gas.

Although the geochemical approach in exploration for gas hydrates seems to be convincing, neither the above mentioned authors nor other publications are specific with regard to compositional and physical parameter determinations. We are also unable to find any references pertaining to the case study where geochemical exploration methods would directly contribute in the discovery of gas hydrate deposits. However we are fully aware that in the Soviet Union, geochemical methods are extensively and successfully used in exploration, particularly for precious and base metals as well as for the conventional type of hydrocarbon deposits. Because of the Russians' leading role in the exploration geochemistry, we are also convinced that the Russian geochemical literature, with emphasis on its application also in the gas hydrate field, should be evaluated separately.

### **Well Logs**

Prior to the discovery of natural deposits of gas hydrates, electric well logs were extensively used in determination of occurrence and depth of the permafrost. In 1958 Dyakonov showed good logging results while measuring temperature of open holes. The applicability of electric resistivity and caliper logs in finding vertical permafrost boundaries has been published by Dostovalov (1955), Akimov (1959), Ostriy and Cherkashin (1960; Figure 27).

Some features of the logs obtained from the intervals of gas hydrates have been presented by Sheshukov (1972), Sapir (1973), Makogon (1974) and Trofimuk, Cherskii, Tsarev, Nikitin (1982; Figures 28 and 29). However, these authors only briefly discuss the response of the gas hydrate intervals to such measurements as: resistivity, spontaneous potential, neutron-gamma and caliper. Because of frequent unusual log responses from gas hydrate zones, the Russian authors recommend using this technique in various combinations.

## CONCLUSIONS

It is beyond the scope of this report to discuss in detail the applicability of gas hydrate formation factors, exploration and development methods emphasized or recommended by Russian professional engineers and scientists. An attempt is made, however, to demonstrate the great number of Russian scientists and institutions involved in gas hydrate investigation. In spite of the considerable difficulties (often because of incomplete bibliographic data or mathematical equations without explanation of used symbols) in proper understanding of the Russian publications, we made efforts to present and evaluate without bias particularly those areas of investigation which most concerned the Russian authors and where they have specific achievements.

Thus, the foregoing information (data base for this report), our conclusions, and recommendations can be outlined as follows:

1. The prevention of hydrate formation in gas transportation systems continues to provide the main impetus for Russian research. Such problems continue to be encountered during production tests in northern areas of the Soviet Union. However, to a lesser degree, they contain factual data obtained from practical application by the industry.
2. From the long list of Russian authors publishing hydrate literature, five have more than five publications. These authors are: Yu.F. Makogon, N.V. Cherskii, V.P. Tsarev, A.A. Trofimuk and V.A. Khoroshilov. Hence, we consider these scientists to represent the main group of Russian gas hydrate researchers.
3. Most hydrate studies are multidisciplinary as reflected in the several names per publication. Theoretical and experimental studies are largely represented by the work of Yu.F. Makogon. A.A. Trofimuk specializes in applications of theoretical findings whereas N.V. Cherskii and V.P. Tsarev have interests in both theoretical and practical aspects.
4. Very few articles discuss the geological factors controlling or related to gas hydrate formation and stabilization.
5. It appears that the process of gas hydrate formation in natural environments is not at all uniform. Except for generally accepted pressure (P) and temperature (T) conditions, some other factors are decisive and should be further studied.

6. Genesis of known continental natural gas hydrate deposits and the suggested formation mechanism of marine hydrates are different from each other. The model(s) which would encompass the entire scope of the hydrate deposits still has not been developed.
7. With regard to marine hydrates we have not found any significant factual data in Russian literature. The available papers are based on general oceanographic, marine geology and theoretical data. Limitations in this field most likely stem from a lack of drilling and core data, particularly from Russian Arctic offshore areas. We also have not noted any Russian seismic sections from offshore areas where bottom simulating reflectors (BSRs) would be present.
8. Thermodynamics and kinetics, although with the principal factors largely adopted from the original investigators (von Stackelberg, 1954, 1956; Katz, 1942, 1944, 1949, 1971; Johns, 1954; McInture and Peterson, 1954), seem to be the strongest domain of Russian scientists-specialists in gas hydrates. Thermodynamics and kinetics of natural gas hydrate formation at a free gas-water interface are relatively well known in qualitative and quantitative terms. Russian science contributed significantly to the understanding of hydrates in a porous medium. The quantitative data from this area however needs more confirmation from the field, particularly from the marine environment.
9. Considering the most recent publications, we conclude that gas hydrate thermodynamics and kinetics research projects are still being continued. Moreover, Barkan and Voronov (1982) emphasize that further investigation in thermodynamics and kinetics is needed in order to solve numerous exploration problems. According to the latter authors, it is particularly important to establish better understanding of the gas vapor pressure and gas diffusion within various zones of the gas hydrates. Gas hydrate kinetics in the context of a sediment pore geometry and capillary system, and water dynamics related to the hydrate zone still have to be investigated.
10. A vast majority of the articles are directly or indirectly related to experimental findings on thermodynamic conditions of gas hydrate formation. The discovery that gas hydrates are a major part of the Messoiaikh field precipitated laboratory simulations of conditions of hydrate formation and destabilization (Makogon, 1970, 1971). The experimental data evoked a series of papers with attempts to apply those findings in the field (Makogon, 1970; Trofimuk, 1979, 1980, and others). However, most of the presented results are very general and mainly framed within a P-T reference, at best.
11. Another topic commonly discussed is estimates of hydrocarbon reserves within gas hydrates in offshore and onshore areas (i.e. Cherskii and Tsarev, 1976). These calculations are based on approximate estimates of the density of gas reserves in gas hydrates in various structural zones of the oceans.



Russian authors came up with the average figure of  $8 \times 10^8 - 10^9 \text{ m}^3$  of gas per  $1 \text{ km}^2$ . They also state that 60% of the natural gas reserves in gas hydrates are concentrated in the Sea of Okhotsk and the Sea of Japan. The adopted amount of gas in marine sediments was 270 to  $700 \text{ cm}^3$  per liter of sediment assuming a porosity of 30 - 50%. In this respect we did not find any numbers based on measurements of gas amounts from gas hydrate cores, which require using hermetic core barrels (PCB).

12. Trofimuk et al. (1982) estimated the continental gas reserves associated with hydrates as  $1.7 \times 10^{13} \text{ m}^3$  ( $61.4 \times 10^{10}$  MCF). The most comprehensive estimate for the oceanic regions are  $3.96 \times 10^{15} \text{ m}^3$  ( $14 \times 10^{13}$  MCF) shelf,  $48.7 \times 10^{15} \text{ m}^3$  ( $17.2 \times 10^{14} \text{ m}^3$  ( $17.2 \times 10^{14}$  MCF) slope,  $424.7 \times 10^{15} \text{ m}^3$  ( $15 \times 10^{15}$  MCF) rise and abyssal plain, after Cherskii and Tsarev (1977).
13. Natural gas hydrate occurrence in offshore areas is poorly represented in Russian literature. It is based entirely on general data of temperature profiles of sea waters, oceanographic surveys of water salinity, and on general thermodynamic conditions of gas hydrate formation (i.e. Makogon, Trofimuk, Tsarev, and Cherskii, 1973).
14. As to the methods of gas hydrate detection, two groups are usually considered:
  - a. Seismic methods. In several articles Russian authors suggest using acoustic means of gas hydrate detection in offshore areas (Trofimuk et al., 1980). Given the laboratory experimental data on elastic wave velocities in gas hydrate zones, they do not present graphic examples of any results based on applied methods.
  - b. Well logging. The log characteristics in gas hydrate zones presented by Yu.F. Makogon (1974) seem to be one of two available sources of information in Russian literature. They are of a very general character and are limited to SP, resistivity, and caliper measurements.
15. Variation of gas content in hydrates leads to the problem of gas hydrate formation in different structural and sedimentological zones of the oceans. Probably the fullest (by Russian standards) model of gas hydrate formation in oceanic areas was given by N.V. Cherskii and V.P. Tsarev in 1977. This model is discussed in the main body of this report (p 16).

Notice that a major part of the model refers to a hydrocarbon generation mechanism. The rate of methane generation is mainly controlled by the mass transfer of source material ( $\text{CO}_2$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$ ) since the rate of their biochemical processing is fairly great. Because of the fact that formation of gas hydrates requires a high level of gas saturation in sea water, the amount of generated methane must be greater than that of dispersed methane. The authors' calculation seems to confirm a higher rate of methane

formation than dispersal. Once the sediments are filled with 70 - 80% hydrates, they become hydrocarbon seals and the formation of ordinary gas deposits begins beneath.

16. Virtually the only and the most specifically described location with gas hydrates is the Messoiakh field (Makogon, 1974; and Sheshukov, 1972). The field was discovered in 1967 in the Yenisei-Khatung trough in the northeastern part of Siberia. The gas and gas hydrate deposits occur in the Dolgan Sandstone Formation and Albian-Cenomanian age, and lie at the depth of about 730 meters. Porosity and permeability of the productive series are 24 - 27% and 125 md, respectively. The formation pressure at the top equals 78 atmospheres while the relative density of gas consisting mainly of methane is 0.56.

Production tests of the top section of Dolgan Sandstones showed very insignificant gas flow with increasing amounts of water (up to 80%) after treatment with inhibitors. The same tests in the lower sections of the pay-horizon turned out to yield significantly larger gas flows. Calculations showed that during the first eight years of gas production 21% of gas hydrates were exploited. As a result of the hydrate dissociation an additional  $3.17 \times 10^9 \text{ m}^3$  of gas entered the formation during the period of conservation.

17. The method of designating the area of possible hydrate formation presented by E.S. Barkan and A.N. Voronov (1982) on the territory of the USSR is in fact a modified method described by Yu.F. Makogon in 1974. The calculations of temperature and pressure necessary for gas hydrate formation were modified with regard to the salinity of water saturated with gas. According to Barkan and Voronov's calculations the area of possible gas hydrate distribution on the territory of the USSR has been estimated to be  $340 \times 10^3 \text{ km}^2$ ; 50% of these entire gas reserves in the hydrate zone are located in the Leno-Vilyui Province.

18. E.S. Barkan and A.N. Voronov disagree with the results of studies by Koblova and Makogon (1971) on the relationship between pressure and water saturation in gas at a given temperature. They suggest another definition of the equilibrium of the three phase (i.e. water-gas-hydrate) system. Surprisingly, Barkan and Voronov's theory in many aspects is based extensively on the principal findings by Makogon and Koblova.

19. The calculation methodology of gas reserves in hydrate deposits is mainly focused on kinetics of gas dissolved in water and its transfer into the hydrate. The method is by no means presented completely, as E.S. Barkan and A.N. Voronov very often refer to other publications which in some instances are hardly accessible. E.S. Barkan and A.N. Voronov admit that previously made projections of gas reserves in hydrate deposits are significantly lower when a more reasonable gas recovery factor of 0.1 (10%) is applied. The same scientists point out the fact that although gas reserves in gas hydrate deposits are very valuable, their production faces tremendous technological problems at the present time.

20. In the Russian literature are also methodologies proposed for gas production from naturally occurring gas hydrates. Generally, the methods appear to be closely similar to those proposed by Western countries' engineers, as follows:
  - a. Gas production on land (permafrost). Russian hydrates on land are found in well indurated sandstones. In situ breakdown may be achieved by either providing energy from the surface (considered to be unprofitable) or using energy latent in the surrounding rocks. One proposed method involves decrease in pressure causing a flow of heat from subjacent horizons of sufficient magnitude to continue the hydrate dissociation. Another method involved the introduction of hot water from subjacent horizons. Water at 50°C or higher is ubiquitous throughout the land regions of hydrate occurrence in the USSR. Estimates suggest that 10 - 25% of this thermal energy should be applied to direct hydrate dissociation and the remaining energy transferred to adjacent non-hydrate bearing zones. Production of gas would be expected 2 to 4 years after the initial heating of the hydrate zone.
  - b. Gas production from marine gas hydrates. Technical plans for the development of hydrates offshore have usually been formulated in terms of mass disturbance of unconsolidated sediment and transport of the resultant slurry (sediment + gas + hydrate) to the surface where gas separation occurs. The Russians consider the upper hydrate zone to be insufficiently hydrate enriched for profitable production. Consequently, hydrate development involves removal of this zone through an excavation program (up to 7 m thick) and development of the productive zones beneath. They consider that the sediments within the producible hydrate zone are sufficiently uncompacted to facilitate mechanical disturbance and removal. They note, however, that production costs appear to be extremely high and would require the recovery of other unspecified "valuable components" to be a profitable venture.
21. The complex nature of the processes that formed enormous gas hydrate concentrations in permafrost regions and submarine environments cannot be deduced completely from a reconnaissance type study. However, review of many publications provides at least partial insight into the gas hydrate formation processes, exploration methods, the degree of success in suppressing gas hydrates where and when they are undesired, and production achievements where the gas hydrates are considered as an alternative energy source.
22. Within this study framework, we can with confidence consider the Messoiak and Vilyui gas hydrate deposits as economically very interesting and probably feasible for industrial operations even with the U.S. development and operations economics.

23. The development and dissociation methods applied in the Messoiakh gas hydrate deposit (dissociating it from the lower hydrate boundary) have to be definitely considered as an achievement.
24. The extremely large gas potential resources (although not yet reserves, Krason and Rudloff, 1985) in the offshore and continental-permafrost environments assessed by Russian authors encourage the continuation of stronger efforts for either verification of already estimated gas resources or their reassessment with the highest possible level of confidence.
25. Although we realize that the literature gathered, studied and evaluated for this report is incomplete, we are confident that our findings factually represent the status of the Russian knowledge in the various branches of the gas hydrate field.
26. The massive pipeline transportation of gas and oil from and/or through arctic regions creates serious problems. A similar situation occurs in transportation of hydrocarbons from some offshore regions. In view of these problems, and present and future exploration interest in energy and mineral resources of marine environments, much closer cooperation in broad field of gas hydrates is recommended among the U.S., the U.S.S.R. and other interested countries. We recommend organizing an "International Symposium on Gas Hydrates." We suggest considering such a symposium to be held first in the Soviet Union, in Norilsk or Yakutsk, with a field trip to the Messoiakh gas hydrate field. Subsequently, a similar symposium could be held in Fairbanks, Alaska, with field trips to permafrost areas potentially favorable for gas hydrate deposits.

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APPENDIX I

LIST OF RUSSIAN AUTHORS AND NUMBER OF THEIR  
PUBLICATIONS RELATED TO GAS HYDRATES  
(1965 THROUGH 1984)

AUTHOR'S NAME	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	TOTAL NUMBER OF PUBLICATIONS
Agishev, A.P.						1															1
Aleksandrov, A.L.								1													1
Aleksandrov, V.K.																1					1
Antonova, G.M.							1														1
Arshinov, S.A.						1															1
Babem, G.D.										1		1									2
Balobaev, V.T.																		1			1
Barkan, E.S.													2					1	1		4
Barmina, E.S.																1					1
Baulin, V.V.														1							1
Belov, V.						1															1
Beniaminovich, A.E.								1													1
Beznosikov, A.F.						1		3													4
Biske, S.F.																	1				1
Blazhchishin, A.I.														1							1
Bodunov, V.A.															1						1
Bogatskiy, V.V.											1										1
Bagatyrenko, R.S.									1												1
Bondarenko, B.M.																	1				1
Bondarev, E.A.										1		1									2
Borodzich, E.V.														1							1
Borovikov, Y.V.																1					1
Byk, S.																1					1
Chadovich, T.Z.														1							1
Cherskii, N.V.						5	1	6	3	4	1	3	2	2	4	1		2			34
Chudov, A.F.															1						1
Degtyarv, B.V.					1			1													2
Demchenko, A.V.		2																			2
Devyatkin, V.N.																		1			1
Dobrynin, V.M.															1						1
Druzhin, V.N.										1											1
Duchkov, A.D.																		1			1
Dunichev, V.M.																		1			1
Ettinger, I.L.										1											1
Fomina, V.A.							3	2								1					6
Fradkin, G.S.																1					1
Gafarova, M.A.														1							1
Galaktynov, B.R.						1															1
Galerkin, L.I.																		1			1

AUTHOR'S NAME	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	TOTAL NUMBER OF PUBLICATIONS
Gelvi, T.N.																	1				1
Ginzburg, G.D.					1				1												2
Gnibidenko, G.S.																	1				1
Golovachev, E.M.																1					1
Gorshkov, A.N.								1													1
Gritsenko, A.I.														1							1
Groysman, A.G.																		1			1
Gurski, Y.N.												1		1							2
Gusein-Zade, M.A.									1												1
Gutsalo, L.K.																	1				1
Hramenkov, Y.H.								1													1
Ibragimova, K.I.								1													1
Ilev, A.Y.															1						1
Iskaderov, S.M.									2												2
Izosimova, A.N.															1						1
Joffe, A.K.																1					1
Kalimov, Y.I.						1															1
Kanibolotskiy, A.													1								1
Kapyrin, Y.V.											1										1
Karotaev, Y.P.					2	1									1						4
Kashirtsev, V.A.															1						1
Khalikov, G.A.						1	1														2
Khoroshilov, V.A.		2			1	1		2	2	3											11
Khramenkov, E.N.								1													1
Khutorskoy, M.I.																1					1
Kislova, V.I.									1												1
Klimanov, V.A.														1							1
Koblova, I.L.							2	1													3
Kolodeznyi, P.A.						1															1
Kontorovich, A.E.																		1			1
Korobeynik, V.M.														1							1
Koshelev, V.S.					1	1	2	1													5
Kosygin, Y.A.																		1			1
Kozlov, A.L.					1																1
Kozlov, N.A.										1											1
Krasnyi, L.I.															1						1
Krasnyi, M.L.														1							1

[illegible]

AUTHOR'S NAME	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	TOTAL NUMBER OF PUBLICATIONS
Popova, A.K.											1					1					2
Razvarin, D.Y.						1															1
Rikhterman, D.L.															1						1
Rogozhina, K.Y.															1						1
Rozenberg, M.D.											1										1
Rusanov, V.P.																	1				1
Sadchikov, P.B.														1							1
Safranov, A.F.															1						1
Sandler, B.N.																	1				1
Saniev, Z.A.								1													1
Sapir, M.Kh.								1	2												3
Sarkis'yants, G.A.		1																			1
Savinikhina, A.V.															1						1
Savinskii, K.A.																1					1
Schlezinger, A.Y.																1					1
Sedov, N.V.														1							1
Selivanovskiy, D.A.																	1				1
Semenov, D.F.																	1				1
Semin, V.N.					1																1
Seslavinsky, K.B.																	1				1
Shapenko, V.V.														1							1
Shaposchnikova, Y.A.														1							1
Shchepetkin, Y.V.														1							1
Sheshukov, N.L.								3	1												4
Shevchenko, V.E.										1											1
Shulman, N.V.										1											1
Sidler, L.E.						1															1
Siemin, V.I.				1		1															2
Skhaliakho, A.S.								1													1
Skorobogatko, A.N.																		1			1
Smirnov, L.F.															1						1
Smirnov, V.S.					1																1
Smirnov, Y.B.										1							1				2
Smyslov, A.A.														1							1
Snegovskoi, S.S.									1						1						2
Sobolev, A.A.												1									1
Sokolov, A.Y.																	1				1
Solovev, A.A.										1	1										2
Solovev, V.A.								1													1

AUTHOR'S NAME	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	TOTAL NUMBER OF PUBLICATIONS
Solovev, V.V.														1							1
Soshnikov, A.E.									1												1
Stadnik, V.K.									1												1
Starobinets, L.S.										1											1
Stupanov, G.P.																1					1
Sumets, V.I.										1											1
Suprunenko, Q.I.								1													1
Surkov, V.S.																		1			1
Svabichevskii, A.S.															1						1
Taboyakov, A.I.															1			1			2
Tchemakin, N.M.																1					1
Tikhomirova, E.S.											1										1
Tkachenko, M.F.						1															1
Tolkachev, M.V.																	1	1	1		3
Trebin, G.F.											1										1
Trebin, F.A.		2					2														4
Trofimuk, A.A.							2	1	3	4	2			1	4	2	2	2	1		24
Trotsyuk, V.Y.														1							1
Tsarev, V.P.						2	2	5	2	4	1	3	5	2	4	1		2			34
Tuezov, I.K.															1						1
Tynsuhnyakova, G.N.									1												1
Tyutrin, I.I.															1			1			2
Umnyakhin, A.S.														1							1
Vakhitov, G.G.											1										1
Varentsov, M.I.										1											1
Vasiliev, B.I.						2			1		1										4
Vashchilov, Y.Y.										1											1
Veselov, O.V.										1											1
Vityaz, V.L.											1										1
Vlasenko, V.I.								1													1
Volkhonin, V.S.																1					1
Volkova, N.A.										1											1
Volodina, L.A.															1						1
Volodko, B.V.																		1			1
Voronov, A.N.																		1	1		2
Yakoviev, Y.T.									1												1
Yakutseni, V.P.														1							1
Yefremov, I.D.						1		1	1												3
Yefremova, A.G.											1										1
Yurin, G.A.									1												1
Zhizhenko, B.P.										1	1										2
Zorkin, L.M.									2												2
TOTAL	2	11	0	1	17	34	24	52	36	40	18	13	15	31	31	22	20	27	7	1	402



APPENDIX II

RUSSIAN PUBLICATIONS RELATED TO THE NATURAL  
DEPOSITS OF GAS HYDRATES  
(1960 THROUGH 1984)

NAMES OF JOURNALS AND PUBLISHING INSTITUTIONS	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	TOTAL NUMBER OF PUBLICATIONS
Bezopasnost Truda v Promishlennosti															1											1
CNTI																										1
Mingazprom							1																			1
Doklady Akademii Nauk SSSR					1							3	4	4	8	7	1	9	1	2	6	2				48
Ekspress - Informatsiia, VNIIE Gazprom											2	3	1								1					7
Fondy IGIRGI, Moscow										1										1						3
Gazovaya Promishlennost						2				2	2	1	2	2	3			3	1	1	1	1				20
Gazovoe Delo							1					2	5													8
Geofizicheskie metody razvedki v Arktike													1					2								3
Geologiya i Geofizika	1												2	1	3	2	1	1	4	1	4					20
Geologiya Nefti i Gaza										1				4		1	2				2	1				11
Geologiya VNIIE Gazprom									1	1			2							1						5

## APPENDIX II (CONT.)

**RUSSIAN PUBLICATIONS RELATED TO THE NATURAL  
DEPOSITS OF GAS HYDRATES  
(1960 THROUGH 1984)**

NAMES OF JOURNALS AND PUBLISHING INSTITUTIONS	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	TOTAL NUMBER OF PUBLICATIONS
International Geological Revue										1																1
Inzh. - Fiz. Zhurnal										1										1						2
Izvestiia Akad.Nauk Kaz.SSR;Seria Khim.													1													2
Izvestiia Ucheb. Zaved,Nefti i Gaz																			1							1
Khimia Tekhnologiia Topliv Masel												1														1
Litologiya i Poleznyye Iskopaemye Nauchno-Technicheski Sbornik-Seria Gazovoe Delo										4								2								2
Nauchno-Technicheski Sbornik-Seria Gazovoe Delo									4																	8
Neft i Gaz						1			1																	2
Neft i Gaz Tiumenii									1												1					2
Oil an Gaz International Priroda									2																	2
Safety Technology, Labor Protection and Mine Reserve											1									1						1

**RUSSIAN PUBLICATIONS RELATED TO THE NATURAL  
DEPOSITS OF GAS HYDRATES  
(1960 THROUGH 1984)**

NAMES OF JOURNALS AND PUBLISHING INSTITUTIONS	TOTAL NUMBER OF PUBLICATIONS											
	1984	1983	1982	1981	1980	1979	1978	1977	1976	1975	1974	1973
Sbornik: Gornoe Delo				1								2
Sbornik:Ekspluatatsiia Gazovykh Skvazhin VNIIOENG												1
Sbornik:Razrabotka i Ekspluatatsiia Gazovykh Mestorozhdenii VNIIOENG					1							1
Sbornik:Trudi Inst. Geol.Razrab.Transp. Trudy Gas.Nauchno- Issled Projektn.Inst. "GIPROYUMEN-NEFTEGAZ"					1	1					1	2
Trudy Instituta Khimii Nefti i Prirodnnykh Solei AN KAZ SSR									2			2
Trudy MINKH:G.P. im.I.M.Gubkina Trudy VNII Prirodnnykh Gazov						1					1	2

APPENDIX II (CONT.)

RUSSIAN PUBLICATIONS RELATED TO THE NATURAL  
DEPOSITS OF GAS HYDRATES  
(1960 THROUGH 1984)

NAMES OF JOURNALS AND PUBLISHING INSTITUTIONS	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	TOTAL NUMBER OF PUBLICATIONS
Zhurnal Fiziches- koi Khimii													1													1
KHIMIYA Izda- telstvo, Moscow																					1					1
NAUKA Press, Novosibirsk																	1						1			2
NAUKA, Moscow											1			1												2
NEDRA, Moscow					1	2				1				1												5
Yakutskoe Knizh- noe Izdatelstvo										1	1	3					1									5
Others										1	1							2								4
TOTAL	1	-	-	-	1	2	6	-	1	11	17	12	22	17	19	9	5	6	15	9	8	12	8	3	1	185